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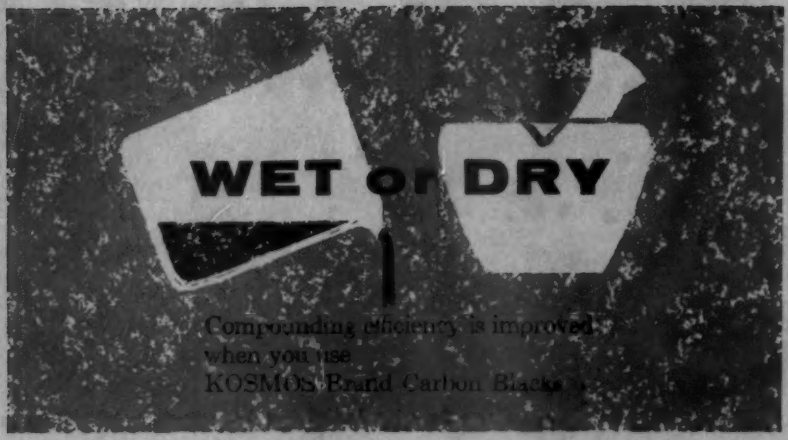

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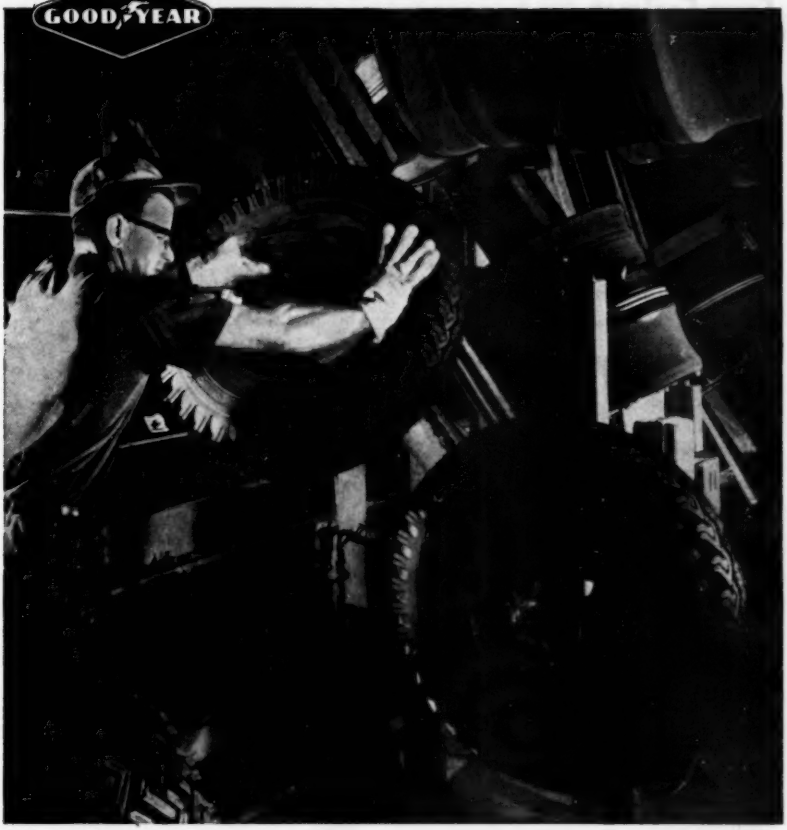

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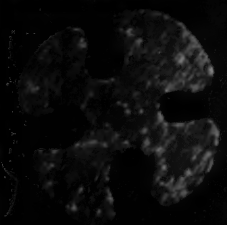

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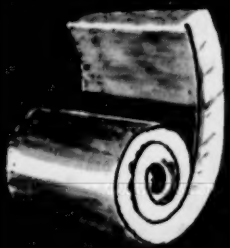

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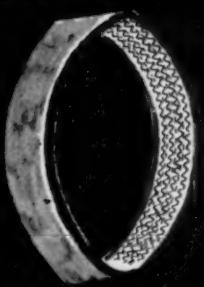

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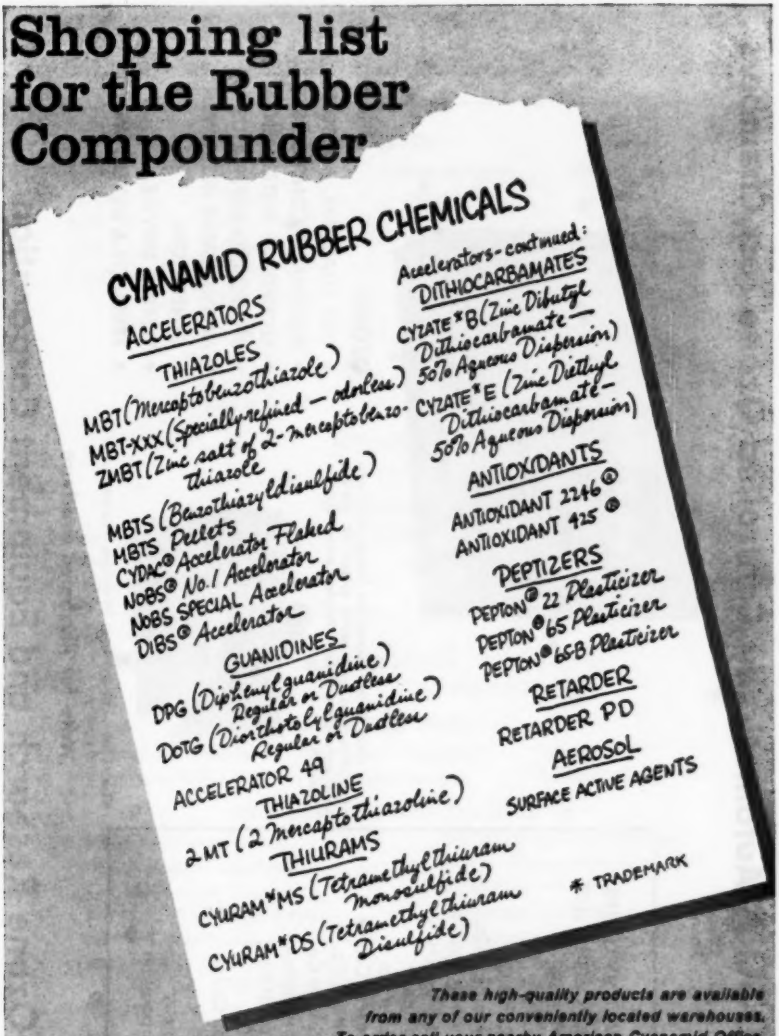

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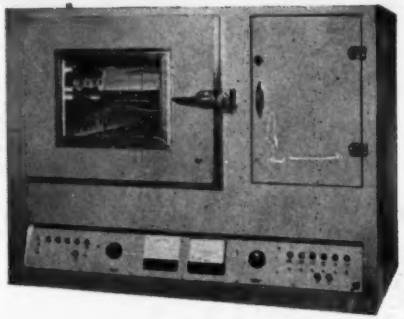

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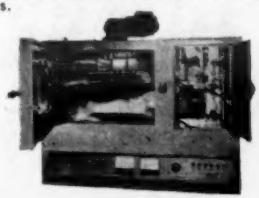

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MBT	Tetrone A	Zenite Special
MBTS	Thionex	Zenite A
	Thionex Grains	Zenite AM

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Antox	Neozone D	Zalba Special
	Permalux	

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Aquarex D	Aquarex MDL	Aquarex SMO
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Rubber Red 2BD	Rubber Blue PCD
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Hylene* M-50	Hylene* TM
Hylene* MP	Hylene* TM-65

PEPTIZING AGENTS

Endor	RPA No. 3 Concentrated
RPA No. 2	RPA No. 6
RPA No. 3	RR-10

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RPA No. 3	RR-10

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ELA—Elastomer lubricating agent

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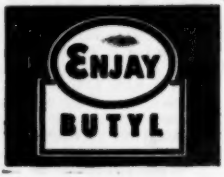

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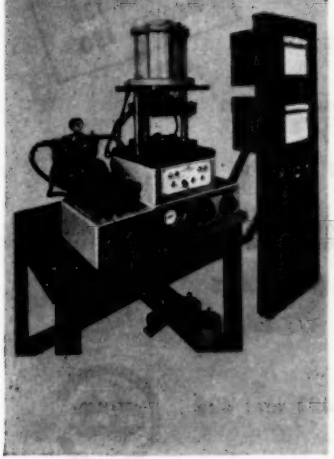

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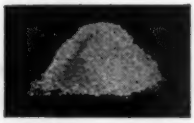

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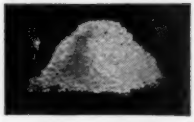

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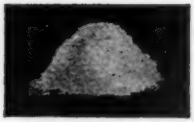

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Los Angeles Rubber Group, Inc.

Chairman: W. M. Anderson (Gross Manufacturing Co., Inc., 1711 S. California Avenue, Monrovia, California). *Assoc. Chairman:* C. M. Churchill (Naugatuck Chemical Division, U. S. Rubber Company, 5901 Telegraph Rd., Los Angeles 22, California). *Vice-Chairman:* L. W. Chaffee (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Treasurer:* J. L. Ryan (Shell Chemical Company, P. O. Box 6066, Lakewood, California). *Secretary:* C. F. Ashcroft (Cabot Corporation, 3350 Wilshire Blvd. #718, Los Angeles 5, California). *Directors:* Don Montgomery (1961–1962), Howard R. Fisher (1961–1962), L. E. Peterson (1961–1962), R. L. Wells (1960–1961), Harold W. Sears (1960–1961), Harold J. Brandenburg (1960–1961), B. R. Snyder (1961). *Asst. Treasurer:* Robert F. Dougherty (U. S. Rubber Company, 5675 Telegraph Rd., Los Angeles 22, California). *Asst. Secretary:* W. C. Scheuermann (Plastic & Rubber Products Co., 2100 Hyde Park Blvd., Los Angeles 47, California). *Historian & Librarian:* Roy N. Phelan (Atlas Sponge Rubber Co., 1707 S. California Avenue, Monrovia, California). *Attorney:* Cecil Collins (2875 Glendale Blvd., Los Angeles 39, California). *Photographer Emeritus:* L. E. Budnick (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Official Photographer:* Bert Sluyter (The Ohio Rubber Company, 6700 Cherry Avenue, Long Beach 5, California). *Director to Division of Rubber Chemistry:* D. C. Maddy (to 1963), Harwick Standard Chemical Company, 7225 Paramount Blvd., Pico Rivera, California. *Officers Tenure:* December, 1960 to December, 1961. *Meeting Dates:* (1961)—February 7, March 7, April 4, May 2, October 3 and November 7.

New York Rubber Group

Chairman: H. J. Peters (Bell Telephone Laboratories, Murray Hill, N. J.). *Vice-Chairman:* R. DeTurk (Cooke Color & Chemical Co., Hackettstown, N. J.). *Sgt.-at-Arms:* W. Birkitt (Passaic Rubber Co., Clifton, N. J.). *Secretary-Treasurer:* R. G. Seaman (Rubber World, 630 Third Ave., New York 17, N. Y.). *Directors:* W. J. O'Brien, Bryant Ross, E. C. Strube, A. H. Woodward, J. T. Dunn, M. A. Durakis, W. R. Hartman, J. E. Walsh, R. T. Ambrose, K. B. Cary, W. C. Carter, A. M. Gessler, E. S. Kern, M. E. Lerner. *Officers Tenure:* January 1, 1961–January 1, 1962. *Director to Div. of Rub. Chem., ACS:* C. V. Lundberg (to 1963). *Meeting Dates:* (1961)—Mar. 24, June

(Summer Outing), Aug. 1, Oct. 20 and Dec. 15. (1962)—Mar. 23, June 7, Aug. (Golf Outing), Oct. 19 and Dec. 14.

Northern California Rubber Group

Chairman: Virgil C. Price (Burke Rubber Company, 2250 South Tenth Street, San Jose 3, California). *Vice-Chairman:* Victor J. Carriere (Mansfield Tire & Rubber Company, 4901 East 12th Street, Oakland, California). *Treasurer:* Gene L. Unterzuber (Oliver Tire & Rubber Company, 1256 65th Street, Oakland 8, California). *Secretary:* Roger H. Thatcher (Union Rubber Company, 1002 77th Avenue, Oakland 21, California). *Directors:* Eugene Gador, Henri Krakowski, Robert B. Stewart. *Officers Tenure:* December, 1960–December, 1961. *Meeting Dates:* January 12, February 9, March 9, April 13, May 11, June 8, September—open date for Summer Outing, October 12, November 9, December—open for Christmas Party.

The Philadelphia Rubber Group

Chairman: R. N. Hendriksen (Phillips Chemical Company, Trenton, New Jersey). *Vice-Chairman:* R. M. Kerr (H. K. Porter Company, Thermoid Division, Philadelphia, Pa.). *Secretary-Treasurer:* H. F. Smith (Naugatuck Chemical Company, 97 Bayard Street, New Brunswick, New Jersey). *Historian:* J. B. Johnson (Linear, Inc., Philadelphia, Pa.). *Executive Committee:* E. C. Brown, K. E. Chester, R. E. Connor, W. J. Macomber, K. F. Quinn, B. VanArkel. *Director to Division of Rubber Chemistry:* R. A. Garrett (to 1962). *Officers Tenure:* January 1, 1961 to January 1, 1962. *Meeting Dates:* January 27, April 28, August 18, October 13, November 3.

Rhode Island Rubber Group

Chairman: Walter Blecharczyk (Davol Rubber Company, Providence, Rhode Island). *Vice-Chairman:* Edwin C. Uhlig (United States Rubber Company, Providence, Rhode Island). *Secretary-Treasurer:* Joseph Vitale (Crescent Wire Company, Pawtucket, Rhode Island). *Board of Directors:* C. A. Damicone, Joseph M. Donahue, Paul Hastings, Vincent Casey, Tom Crosby, Harry Ebert. *Dir. to Div. of Rubber Chemistry, ACS:* R. W. Szulik (to 1962). *Officers Tenure:* January 1, 1961–January 1, 1962. *Permanent Historian:* Robert Van Amburgh. *Meeting Dates:* April 6, June 8 and November 2.

Southern Ohio Rubber Group

President: Howard G. Gillette (Precision Rubber Prod. Corp., Dayton, Ohio). *Vice-President:* E. N. Ipiotis (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Secretary:* John H. Woodward (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Treasurer:* Donald R. Strack (Inland Mfg. Division, G.M.C., Dayton, Ohio). *Directors:* F. W. Gage, Harold Schweller, D. L. Allen, C. Bellanca, R. Heist, R. L. Jacobs, M. K. Coulter, J. West, H. S. Karch, W. F. Herberg, J. M. Williams. *Director to Division of Rubber Chemistry:* H. E. Schweller (1962). *Officers Tenure:* January 1, 1961–January 1, 1962. *Meeting Dates:* March 23, June 3, September 28 and Dec. 9.

Southern Rubber Group

Chairman: Lenoir Black (C. P. Hall Company, 648 Riverside, Memphis, Tennessee). *Vice-Chairman:* Roswell C. Whitmore (3610 Waldorf, Dallas,

Texas, (Better Monkey Grip Company)). *Secretary:* R. W. Rice (Firestone Synthetic Rubber & Latex Company, Box 21361, Lake Charles, Louisiana). *Treasurer:* Martin E. Samuels (Copolymer Rubber & Chemical Corp., Box 2591, Baton Rouge, Louisiana). *Officers Tenure:* June, 1960–June, 1961. *Meeting Dates:* (1961)—January 20–21; June 23–24; November 17–18 and (January 26–27, 1962).

Washington Rubber Group

President: Philip Mitton (Materials Branch, U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia). *Vice-President:* Thomas A. Tharp (General Tire & Rubber Company, 1120 Conn. Avenue, N. W., Washington, D. C.). *Secretary:* Daniel Pratt (Code 634 C, Bureau of Ships, Navy Department, Washington 25, D. C.). *Treasurer:* George G. Richey (National Bureau of Standards, Washington 25, D. C.). *Director to Division of Rubber Chemistry:* A. T. McPherson (to 1961). *Officers Tenure:* July 1, 1960 to July 1, 1961. *Meeting Dates:* January 25, March 8, April 19, May 17.

THE CHEMICAL INSTITUTE OF CANADA RUBBER DIVISION OFFICERS AND SPONSORED RUBBER GROUPS

Chairman: A. Jaychuk (Goodyear Tire & Rubber Co. of Canada Ltd., New Toronto, Ontario). *Vice-Chairman:* D. W. Hay (Polymer Corporation Limited, Sarnia, Ontario). *Secretary-Treasurer:* C. M. Croakman (Columbian Carbon of Canada, Toronto, Ontario). *Directors:* A. Holden (Canada Colors & Chemicals, Montreal, Quebec). W. A. Cline (Canadian General Tower Limited, Galt, Ontario). W. J. Nichol (Dunlop Canada Limited, Toronto, Ontario). *Ontario Rubber Group Representative:* W. R. Smith (Dominion Rubber Company Limited, Kitchener, Ontario). *Quebec Rubber & Plastics Group Representative:* J. M. Campbell (Northern Electric Co., Lachine, Quebec).

The Ontario Rubber Group

Chairman: D. G. Seymour (Cabot Carbon of Canada Ltd., Toronto, Ontario). *Vice-Chairman:* W. R. Smith (Dominion Rubber Company Limited, Kitchener, Ontario). *Secretary:* L. V. Lomas (c/o L. V. Lomas Chemical Company, Toronto, Ontario). *Treasurer:* Bruce Williams (Feather Industries Limited, Toronto, Ontario). *Membership Chairman:* W. J. Hogg (Naugatuck Chemicals Division, Dominion Rubber Company Limited, Elmira, Ontario).

Quebec Rubber & Plastics Group

Chairman: J. M. Campbell (Northern Electric Company, Lachine, Quebec). *Secretary:* L. V. Woytiuk (Northern Electric Company, Lachine, Quebec). *Treasurer:* R. B. Pilmer (Dominion Rubber Company, Mechanical Division, Montreal, Quebec). *Committee Chairmen—Speakers:* F. R. Moorehouse (Shawinigan Chemicals Limited, Montreal, Quebec). *Membership:* R. Vincent (Dominion Rubber Company, Montreal, Quebec). *Publicity:* R. E. Suksi (Sun Oil Company of Canada Ltd., Montreal, Quebec). *Education:* G. L. Bata (Carbide Chemicals Company, Montreal, Quebec). *House Committee:* W. L. Leach (Cabot Carbon of Canada Limited, Montreal, Quebec). *Directors:* W. M. Schwenger (Dupont Company of Canada, Montreal); A. S. MacLean (Dominion Rubber Company, Montreal).

NEW BOOKS AND OTHER PUBLICATIONS

THE APPLIED SCIENCE OF RUBBER. Edited by W. J. S. Naunton. Edward Arnold Publishers, London. $32.50.—This volume is an illustration of the wisdom of a decision made by the Division of Rubber Chemistry in 1956 a part of which was that it was no longer possible to incorporate in a single volume all that needs to be said on the various aspects of this subject because of the rapid burgeoning of the science and technology of rubber. The second part of the decision included the proposal to accomplish this job piecemeal by publishing reviews of a limited number of areas yearly as Rubber Reviews. The experience of four years with this procedure has demonstrated the soundness of this approach. The appearance of this volume underlines it.

It was obviously the intention that this volume be an up-to-date version of Davis and Blake (Chemistry and Technology of Rubber, 1937) and Whitby (Synthetic Rubber, 1954). The editor states in the Foreword that it was necessary to shorten many of the contributions in order to keep the book within reasonable bounds. It is apparent from a perusal of the book that certain areas are treated much too briefly. For example only 50 pages are used to cover synthetic rubbers. There is no adequate treatment of the technology of tires although an adequate treatment of the testing of tires is included. On the other hand there is a long and excellent review of the technology of rubber mountings, springs, etc. a much less important subject than tires. In the chapter dealing with physical testing there is no discussion of tests relating to processability and specifically none for the very important measurement of scorch although a mention is made of the Vulcameter and the English version of this device, the Curometer, as methods for determining "optimum" cure. There is no mention made in this chapter nor elsewhere of the Mooney Plastometer (although there are two figures showing Mooney cure curves on pp. 364 and 372) which is so widely used throughout the world. There is no discussion whatever of adhesives or adhesion although there is a brief dicussion of testing of bonded units.

Inevitably in a work of this scope there is an uneven quality in the style and the method of presentation which varies from excellent to poor. There are also some duplications (optimum cure is discussed in several places) and a few errors some of which are as follows:

In Part I of the chapter on synthetic rubber under *Bulk Polymerization with the Alkali Metals* the author implies in reference (9) that the Goodrich-Gulf process was identical with the Firestone process, i.e., using lithium catalysis. (The names of the authors are badly mangled in this reference. Alliger becomes Allinger, Horne becomes Home, Shipman becomes Chipman, and Folt becomes Holt). On the next page under *Other Ionic Polymerizations* it is stated that the announcement of the Goodyear Tire and Rubber Company that a *cis*-polyisoprene had been synthesized using a Ziegler catalyst is regarded as an important step forward. For the record the dates on which these announcements were made and their substance are as follows:

Dec. 13, 1954—Goodrich-Gulf Chemicals Inc. announced the synthesis of a duplicate of natural rubber employing a Ziegler catalyst.

Aug. 22, 1955—Firestone Tire and Rubber Co. announced the synthesis of a rubber closely approximating natural rubber employing lithium as the catalyst.

Oct. 24, 1955—Goodyear Tire and Rubber Co. announced the synthesis of a polyisoprene duplicating the structure of natural rubber using a Ziegler catalyst.

Chapter XII—Part 2 contains a table of product defects, their cause and remedy, which is an excellent idea. One wishes that this had been extended to an entire chapter with more discussion of the reasons for the defects. The cause cited for cracks at mold or backrinding is incorrect but the correct explanation can be found on pp. 318 and 319 in the excellent chapter by J. R. Scott on Fundamentals of Processing.

On p. 722 under a discussion of Set and Creep tests it is stated that in determining compression set whether under constant load (fixed stress) or constant deflection (fixed strain) the set is calculated by expressing the residual strain as a percentage of the original height. This is the case for the constant load test but both the ASTM and BS methods for the constant deflection test require that the set be expressed as a percentage of the deflection imposed.

A statement is made at the bottom of p. 735 that while all other dead weight hardness testers do not give data correlatable with an instantaneous Shore hardness the International Rubber Hardness Method does. This is not the case except for rubbers exhibiting low creep. This particular dead weight test is no different in this respect from other dead weight testers.

On p. 1078 it is stated that the bladder for use in a Bagomatic cure "is made from Butyl accelerated by dimethylolphenol—." The phenol aldehyde resins are vulcanizing agents, not accelerators.

Certain portions of the volume were examined only cursorily, e.g., Chapters I and XI, since this reviewer does not feel qualified to review them. However there are two general conclusions that seem inescapable about the volume as a whole: (a) the quantity of material required for a comprehensive coverage of the subject is now so great that it cannot be contained in a single volume, and (b) the time lag between writing and publication is inevitably so long, perhaps 4 or 5 years, that some of the material becomes obsolete before publication. By A. E. Juve.

SILICONES. Edited by S. Fordham. Published by Philosophical Library Inc., 15 East Fortieth Street, New York 16, N. Y., Hard cover, $5\frac{1}{2} \times 8\frac{1}{2}$ inches, 252 pages, 8 plates, Price $10.00.—Witnessing the rapid and continuing development of the silicone industry, no less than six books devoted to silicone technology have appeared in the English language in the last fifteen years. The most recent is the contribution of a group of British specialists in silicone technology. This authoritative book is intended to give the chemist sufficient information about silicones to enable him to judge potential application for new developments in this rapidly growing field.

The content of *Silicones* is divided into two sections. The first, which may be used as reference by the general reader, gives a condensed account of organosilicon chemistry and discusses the structure and physico-chemical properties of siloxanes. The second section is concerned with the technology of silicones. A discussion of markets which are presently available for silicones is followed by a detailed description of the industrial production of organochlorosilanes and their conversion to silicone fluids, gums, and resins. Silicone fluids, rubbers, and

resins then are covered in three separate chapters. Details of their preparation, composition, and structure are considered with respect to their properties and uses. Helpful comparisons of properties are made with their non-silicone counterparts. The final chapters consider applications of silicones based on special properties such as their water repellency.

Of greatest interest to readers of this journal will be the chapter (thirty-nine pages) on silicone rubbers. Topics covered include gums, fillers, curing agents, processing characteristics of the compounded stocks, and physical properties and applications of the cured rubbers. The discussion is amply supported by data which is clearly presented in tables and graphs. A possible criticism may be the omission of some developments announced in the last few years. For instance, cyanosilicones are omitted from the discussion of oil and fuel resistant rubbers.

The editor of *Silicones* can be commended for gathering the contributions of a number of writers into a well organized and very readable book. Some readers may be disappointed that some recent developments have not received greater attention. Unfortunately, this book is considerably higher priced than its predecessors. By R. E. Frost.

VISCOELASTIC PROPERTIES OF POLYMERS. John D. Ferry. 1961. John Wiley and Sons, Inc. New York. $6 \times 9\frac{1}{4}$ inches, 482 pages. $15.00.—The preface of this book, except for two paragraphs which are here omitted, reads as follows:

It is interesting to observe the evolution of science in microcosm by following the development of a highly specialized fragment of it, especially one which cuts across several conventional fields, such as the subject of this book. The familiar pattern of alternation between experimental and theoretical advances is apparent. Underlying each advance is a conceptual scheme which is an arbitrary and subjective choice of one investigator or school; in this conceptual abstraction, attention is focused on certain aspects of observed behavior that are believed to be particularly important or useful to describe, and other aspects are ignored. The conceptual scheme leads to a set of characteristic physical quantities which can be defined, measured, and correlated by theoretical relationships.

Naturally, in the spontaneous development of the subject, alternative conceptual schemes arise, each with its favored definitions, parameters, and terminology. Sometimes the languages are readily translatable, in other cases with extreme difficulty. In the course of time, a majority of the scientific community may adopt one scheme and for a while a degree of order prevails.

The subject of the viscoelasticity of polymers has not quite reached this last stage of development, but it has matured to the point where some kind of summarizing treatment seems desirable. The phenomenological theory of linear viscoelasticity is essentially complete. The molecular origin of some aspects of the viscoelastic behavior peculiar to polymers is semiquantitatively understood, as are their dependences on temperature, molecular weight, concentration, and other variables. Moreover, the relationships are well enough understood to permit rule-of-thumb predictions of behavior in practical situations to a far greater greater extent, I believe, than has been exploited up to now. Other aspects such as the effects of molecular weight distribution and the properties of highly crosslinked, glassy and crystalline polymers are very poorly understood, but the direction which further experimental and theoretical developments should make is fairly clear.

This book was written with several objectives in view. First, I have tried to assemble the working information needed by investigators in the field, for making measurements and interpreting data—information which has hitherto been scattered in dozens of separate publications. A uniform notation has been used, most of it in accordance with the recommendations of the Society of Rheology. Second, the exposition is I hope straightforward enough so that new investigators, of whom there are many in industrial laboratories encountering the phenomena of polymer viscoelasticity without any previous experience, can use it to familiarize themselves with the subject. Third, certain needs for further theoretical and experimental advances are pointed out. Finally, a few examples of practical applications are given in the hope that these will stimulate a much wider use of approximate interconversions of viscoelastic functions, and reduced variables describing effects of temperature, pressure, and concentration, to predict viscoelastic behavior and correlate it with other properties under a wide variety of conditions.

VISCOELASTICITYS PHENOMENOLOGICAL ASPECTS. ED. J. T. BERGEN. Academic Press. New York and London, 1960. (x + 150 pp.; 9 in. by 6 in.), $6.00. —The symposium, of which this book gives the proceedings, was held at the Research and Development Center of the Amstrong Cork Company, Lancaster, Pa., in April 1958. It was thought appropriate to hold a meeting on this subject at an industrial establishment. While it is debatable whether the theory of the rheological behavior of real materials can yet be of much value in the study of particular industrial processes, a great deal of experimental work is being done which deserves consideration in terms of current theory. Of the seven papers constituting the work, five are in fact reviews, two dealing with mathematical aspects of viscoelasticity, and three with the experimental approach to the subject. In the short space available, none of these can claim to be complete. E. H. Lee deals with stress analysis for viscoelastic bodies in general; J. L. Ericksen reviews the theories of the behavior of certain viscoelastic materials in laminar shearing motions in particular; and H. Markovitz reviews the normal stress effect in polymer solutions, in theory and experiment. In the preface, the editor maintains that the theme of the symposium is 'phenomenological viscoelasticity,' rather than the consideration of molecular models. It is therefore puzzling to find R. S. Marvin's review of the linear viscoelastic behavior of rubberlike polymers and its molecular interpretation. The remaining review paper is of a special kind. J. D. Ferry and K. Ninomiya have compiled from the literature nine different functions related to each of seven typical polymer systems. In many cases, it was necessary to perform interconversions of functions to fill gaps in the data. It is a pity that there appears to be so little order in the results of so much labour, although the general effects are clear enough. Again we have molecular structure discussed in some detail.

The book is completed by R. S. Rivlin and J. T. Bergen, who give two complementary papers, devoted to their own work: 'The constitutive equations for classes of deformations,' and 'Stress relaxation of polymeric materials in combined torsion and tension.'

One is left with the impression that if the aim of the symposium was to provide a review of the subject, then its proceedings would have been better left in the hands of one author; and that the original papers would have been more readily accessible in the appropriate journals. By M. F. Culpin in *Polymer*.

COMPOUNDING INGREDIENTS FOR RUBBER. Rubber World Editors. 1961. Bill Brothers Publishing Co., New York. $15.00.—The following paragraphs are from the introduction.

This edition follows the general style of classification of rubber compounding ingredients which has evolved throughout the world in the various books that have tried to divide these ingredients into some logical order. It has always been difficult, and is becoming more so, to assign one classification to the materials which fulfill more than one function in rubber technology. We have, therefore, set up certain categories and have listed materials in these categories quite arbitrarily in many cases. Our aim has been to satisfy the needs of the user at this point in rubber technology history without making the book too difficult to follow or being too precise in terminology. The materials in this book have been listed in the section (or sections) that fits the major usage as suggested by the supplier of that material. We suggest that categories containing similar types of materials to the one being researched be considered as further sources of possible materials.

A major change in the style of this edition over its predecessor lies in the elimination of text passages which explain how, when, and where to use the type of material under consideration. The editors of this book are convinced that a basic instruction book on the use of rubber compounding ingredients would be of great use throughout the industry but felt that combining a rubber technology text book with this ingredient listing book would be too big an undertaking at one time and would only result in delaying the entire project.

The hazy line of demarcation between "rubber" and "plastic" materials and their uses, and the lack of real satisfactory definitions for these terms, have also meant that we have had to be arbitrary in qualification for inclusion as rubber ingredients and disqualification as plastic ingredients. We have undoubtedly made decisions that could be disputed but our intent was to exclude all materials used exclusively in rigid plastics but to allow some materials used in flexible plastics (and possibly in rubber) to be included.

In the period since the second edition (1947) great changes have taken place in this industry. Synthetic rubber has acquired a major position, not only as a substitute, but as the preferred material for many specific uses. Many new types and grades of synthetic rubber have appeared including commercial production of the stereospecific poly-isoprene and poly-butadiene or "synthetic naturals."

This has been a period of great change in the supplier picture to the industry. Many old company or product names have disappeared due to merger, failure, or just lack of use in rubber. Many new names and products have come along at the same time, although even with a great number of products offered, the number of actual suppliers has dwindled.

MICROSCOPY OF RUBBER. By C. H. Leigh-Dugmore. Published by W. Heffer and Sons Ltd., for the Institution of the Rubber Industry, 4, Kensington Palace Gardens, London, W. 8, England. $6 \times 8\frac{1}{4}$ in. 72 pp. $4.25. (Copies available from *Rubber Age*.)—This monograph, prepared as a short summation of the ways in which microscopy can be used in rubber science and technology, is essentially a survey of work done in the field over the past fifty years. This breadth of scope, the numerous research reports available for reference, and the imposed brevity distinctly limit the amount of specific information the volume

contains. It is not intended as a handbook of rubber microscopy but rather an introduction to the potentials of the field. Microscopy, as here used, covers the entire family of instruments now available: visible-light, ultraviolet, electron; polarizing, dark-field, and phase contact. Natural rubber, the synthetic rubbers, and some elastomers on the borderline between rubbers and plastics come in for mention. The volume is simple in structure and well organized. Following a brief historical survey of microscopy in rubber research, the author outlines the available techniques for examining specimens; a chapter on inspection of polymers and compounded materials, and a concluding chapter on the properties of rubber comprise the work. Many of the techniques of rubber microscopy are not unique to the rubber industry, and these are mentioned only in passing. Those which are distinctive are described briefly, limitations mentioned, suggestions offered for improved results and no more. In the words of the author, "The value of microscopy depends as much on the experience of the microscopist in interpreting what he sees as on his ability to prepare his specimens well, and to operate his microscopes efficiently."

This book is written as a guide, then, showing the microscopist where, and how, to look for such experience. [From the *Rubber Age.*]

NEWER SYNTHETIC RUBBERS DERIVED FROM OLEFINS AND DIOLEFINS *

J. D. D'IANNI

THE GOODYEAR TIRE AND RUBBER COMPANY, AKRON, OHIO

I. INTRODUCTION

Synthetic rubbers are of significant interest to the petroleum industry, since nearly all of the raw materials required in their production are petrochemical in nature. Many of these petrochemicals are produced in large quantities for other chemical end uses as well. Among the most important of these large-tonnage intermediates are butadiene, styrene, acrylonitrile, chloroprene and isobutylene. The newer developments in synthetic rubber, to which this paper will largely be devoted, have focused greater attention on other monomers, such as isoprene, ethylene and propylene.

The following figures will give some idea of the present and future consumption of these raw materials, largely based on petroleum, for chemical manufacture[42, 50]:

PETROCHEMICAL CONSUMPTION ESTIMATES, MILLIONS OF POUNDS

	1960	1965
Ethylene	5000	6500
Butylenes	3420	3980
Propylene	2259	3054
Acetylene	760	995
Butadiene*	1990	2250
Styrene*	1600	1900

* These are production, rather than consumption, estimates.

In the field of elastomers, a close working relationship has existed for many years between the rubber and petroleum industries. In some cases a petroleum company supplies monomers and other raw materials to a synthetic rubber plant operated by a rubber company, often by pipe line on an over-the-fence basis. In other cases the relationship is even closer because the manufacture of both monomer and polymer has been undertaken as a joint venture by a rubber company and an oil company.

Another close association arises from the fact that a large portion of the SBR (styrene-butadiene rubber) made in 1960 was in the form of "oil-extended" rubber, in which 37.5 to 50 parts of a petroleum oil (special lubricating, or light mineral type) per 100 parts of polymer had been added to the latex prior to coagulation. The Rubber Manufacturers' Association predicted that about 200,000 tons of oil, or about 1.5 million bbl., would be used in 1960 for this purpose[55]. Somewhat lower figures are given in another study covering the use of rubber process oils in the period 1951–1967[58].

* Presented at the symposium on "Monomers and Polymers from Petroleum", jointly sponsored by Division of Petroleum Chemistry and Division of Polymer Chemistry, American Chemical Society, at the March 22–25 Meeting 1961, St. Louis, Missouri.

Research and development efforts on elastomers are rapidly increasing each year and have resulted in significant advances in both the science and technology of rubber. It is for this reason that in 1960 it was possible for this country to satisfy nearly 70% of its rubber requirements with synthetic elastomers of all types.

The workhorse of the industry is SBR, which is slowly but steadily improving under the impact of advancing technology. Current interest is centered in such improvements and modifications as carbon black masterbatches, increased oil in "oil-extended" rubber, oil-black masterbatches, and lighter colored rubbers of all types for non-staining uses[73, 183]. This review, however, will concern itself not so much with established products as those which are still in the research and pilot plant stage, and offer considerable promise for early commercialization. Review of progress in the field of elastomers is a popular subject and has resulted in the publication of a number of papers[73, 90, 91, 108, 165, 169, 174, 178]. Many phases of the latex masterbatching process have been covered in a comprehensive review paper[80].

Before research findings on a new elastomer can be applied, it is necessary to work out scale-up problems in its manufacture, and obtain laboratory data on its physical properties and processing characteristics. The utilization of pilot plant facilities has been described with respect to the evaluation of new sources of materials (emulsifiers, extending oils, antioxidants) for emulsion polymerization processes for SBR and nitrile synthetic elastomers[104]. It is emphasized that the complexity of scale-up problems associated with these colloidal systems is still a real challenge to chemical engineers engaged in elastomer development work. Laboratory evaluation of the processing properties of SBR and nitrile rubbers is greatly aided by a study of power consumption curves as determined in a laboratory banbury mixer[57]. The Rotomill[97], a continuous mixing device, and other new processing techniques for the factory have been described[94].

II. DIENE ELASTOMERS

1. *cis-1,4-Polyisoprene.*—The recent discovery and development of stereospecific catalysts have resulted in an intensive investigation of dienes and olefins as raw materials for new synthetic rubbers and plastics. One of the most interesting is *cis*-1,4-polyisoprene since it so closely simulates natural rubber in structure and properties. Early developments in this area have been reviewed[76], but much additional work has since been reported or reviewed[12, 13, 19, 22, 23, 29, 56, 88, 96, 109, 154, 176]. In a symposium at Bad Nauheim, Germany ,discussions were held on a wide variety of stereo rubbers, such as polyisoprene and polybutadiene; ethylene/propylene copolymers, and terpolymers of ethylene, propylene and butadiene[46].

The interest in this new rubber has naturally stimulated a great deal of work on isoprene monomer, which has been available in limited quantities primarily for the manufacture of butyl rubber. These commercial requirements have been met with isoprene produced by steam cracking of naphthas, but the 95% purity of this isoprene is entirely inadequate for the rigid specifications required in stereospecific polymerizations, for which the impurities must be reduced to levels of a few parts per million. At the same time, if *cis*-polyisoprene is to become a commercial venture, Dinsmore has emphasized that isoprene must be produced at a low enough cost so that the polymer will remain competitive with natural rubber at a market price of 25¢ per pound or less[78].

A number of processes for the commerical production of isoprene have been discussed[6]. Dehydrogenation of isopentane is faced with certain problems, such as the formation of substantial amounts of piperylene, as well as acetylenic impurities which are difficult to remove. Methylbutenes as dehydrogenation charge stock do not seem to produce as much of these undesirable byproducts. There seems to be some advantage as claimed in a Shell patent, in simultaneously charging butylenes and isopentenes to produce a mixture of butadiene and isoprene which are readily separable[53]. A new extraction process by Sinclair offers promise for the economical production of high purity isoamylenes from the C_5 fraction of gasoline obtained by catalytic cracking[49].

A two-step process has been under pilot plant study by the Institute Francais du Petrole. Isobutylene (either pure or in dilute form as a butane-butylene refinery stream) and formaldehyde react to form 4,4-dimethyl-*m*-dioxane, which is decomposed over a solid catalyst to isoprene, water and formaldehyde (which is recycled).

Another process under study for commercialization is based upon methylpentenes, predominantly 2-methyl-1-pentene, formed in high efficiency from a refinery propane-propylene stream. The 2-methyl-1-pentene is isomerized to 2-methyl-2-pentene, which is subsequently cracked to isoprene of very high purity suitable for stereospecific polymerizations.

Shell Chemical produces a polyisoprene on a small commercial scale (five tons per day) and markets it as "Shell Isoprene Rubber". Larger construction facilities are being provided for a 20,000 tons/year plant during 1960[54]. The catalyst has not been publicly identified, although some reports indicate it to be butyl lithium[26, 28, 31, 35, 39]. The Shell rubber is stated to have the following characteristics: 92% *cis*-1,4 content; intrinsic viscosity of 8; weight average molecular weight of 2,500,000; Mooney viscosity of 55; ash content of 0.4% (chiefly calcium compounds); and it contains a non-staining antioxidant[95].

Reports have been issued on the research and pilot plant efforts on other isoprene rubbers, such as the Goodrich product Ameripol SN[43, 98, 157], Goodyear's Natsyn[20, 37, 109, 179], and Firestone's Coral Rubber[1, 2, 14, 21, 38, 81, 163]. It is evident from the tremendous amount of research and development work in this area that *cis*-1,4-polyisoprene is to become a commercial synthetic rubber of the first magnitude within a very short time.

Similar research and development investigations are reported underway in Russia, with the first news of the Russian synthesis of a "natural" rubber appearing in 1956[15, 19]. The Russian polymer is referred to as "SKI" polyisoprene rubber (made with a lithium type catalyst) and numerous publications have reported its properties and listed test data[7, 60, 66, 79, 100, 106, 166]. In general, "SKI" appears reasonably similar but not identical to natural rubber in structure and physical properties. Lithium, butyl lithium, and Ziegler-type catalysts (mixture of triethyl aluminum and titanium tetrachloride) have been employed by the Russians in their research work[61, 62, 63, 101, 102, 147]. A rapid scale-up of this development is anticipated, since a pilot plant with a capacity of 1500–2000 tons/year was reported in operation in 1958, and the Russians have established as their objective 25% of total tire production in 1965 to be based on the new isoprene rubber. Copolymerization of butadiene and isoprene in the presence of butyl lithium was studied[147]. Although isoprene, separately, polymerized three times more rapidly than butadiene, in copolymer systems butadiene was the more active monomer.

Recent papers emphasized the specificity and sensitivity of polymerization with stereospecific catalysts[143, 154]. Extreme care must be exercised to eliminate

air, moisture, and polar materials such as alcohols, ethers, ketones, esters, etc. which might either destroy or deactivate the catalyst. Many catalysts can be used, but each is very specific in the type of polymer it will produce.

The selection of a catalyst must still be done largely on an empirical basis, since very little is yet known of the actual mechanics of catalysis. Perhaps determination of the crystal structure of the catalyst will help in predicting the kind of polymer it will be able to produce. One study indicated that the solids obtained upon mixing titanium tetrachloride with aluminum alkyls are complexes of organo-aluminum compounds with the lower titanium chlorides[69].

Much remains to be learned about the true mechanism by which stereospecific catalysts are capable of forming such highly ordered polymers as *cis*-1,4-polyisoprene. The catalysts obtained from aluminum alkyls and titanium tetrachloride have been studied[99, 153]. When these components of the catalyst complex are mixed, a solid precipitate formed which contains practically all of the titanium in a reduced valence state. As the amount of aluminum alkyl used increases, the solid changes from brown $TiCl_3$ to other compounds in which the chlorine is partially replaced by alkyl groups. The rate of polymerization depends on the Al/Ti ratio, with a maximum rate at a 1:1 mole ratio to give the desired *cis*-1,4-polyisoprene, and a secondary maximum at 1:3 to yield a resinous polymer. The inherent viscosity of the polymer increases with conversion to a point and then levels off. From a kinetics standpoint, the reaction is first order in monomer concentration with an activation energy of about 14.4 kcal/g-mole at constant Al/Ti ratio and constant catalyst level. The overall reaction can be represented as

$$-dm/dt = k\,[M][AlR_3][TiCl_4]$$

which agrees with a proposed Langmuir-Hinshelwood type of mechanism. Similar kinetic studies on the polymerization of butadiene have been reported[92].

The mechanism of polymerization of isoprene by Ziegler-type catalysts is very likely of the anionic type[76, 88]. Growth of the polymer chain can be visualized as taking place by the insertion of polarized, oriented molecules of monomer between the growing chain and the surface of the catalyst. The highly unsaturated monomer is more strongly oriented and absorbed on the surface of the catalyst than the polymer molecule. Chain termination occurs by transfer of a hydride ion to the catalyst, or by chain transfer with a molecule of monomer. A comprehensive theoretical study of the mechanism of Ziegler-type polymerizations has been published[175].

The mechanism of polymerization with a lithium catalyst has also been studied, and the ability of lithium (but not the other alkali metals) to exert a stereospecific effect is attributed to its ability to behave as if it were divalent[163]. A complex, it is theorized, is formed between a carbon-bound lithium atom (at the end of a growing polymer chain) and the *cis*-form of isoprene monomer. The complex rearranges to an activated form represented by a six-membered ring, which upon opening results in extension of the chain by head-to-tail addition of *cis*-isoprene units. The proposed mechanism can be described as the addition of a diradical to a polarized but covalent carbon-lithium bond.

The structure of polyisoprene prepared with alkali metal catalysts (lithium, sodium, potassium and some of their organoderivatives) is dependent upon the metal and solvent employed[171, 167]. The nature of the propagating ion pair ($\sim\sim$ isoprene$^-$ M^+) is largely determined by the counterion M^+ and the type of solvent. The ionic character (or degree of charge separation) of this pair seems to determine to a large degree the structure of the polymer. If there is a

large charge separation, as would be expected in solvents such as diethyl ether and tetrahydrofuran, all initiators produce polymers with structures comprising 1,2-, 3,4- and *trans*-1,4-adducts. To obtain a high *cis*-1,4-structure, a system with the least charge separation (i.e., lithium in a hydrocarbon solvent) must be employed.

Another interesting correlation by Tobolsky and Rogers[170] in a study of styrene-isoprene copolymers is that highly ionic systems (i.e., Na in ethers) produce copolymers of high styrene and low 1,4-adduct contents, while less ionic systems (i.e., butyl lithium in aromatic ethers or hydrocarbons) result in copolymers of lower styrene and higher 1,4-adduct contents.

A review of recent developments in anionic polymerization emphasizes that the two outstanding features of the reactions of carbanions with monomers are stereospecificity and absence of chain termination[121]. The former has made possible the synthesis of polymers of regulated chain structure through the use of stereospecific catalysts (Ziegler-Natta or lithium type). The latter has permitted a high degree of control over the molecular weight distribution of the polymer. In the case of isoprene polymerization with an alkyl lithium, the reaction appears to be greatly influenced by the formation of polymer ion pairs (RLi) and catalyst ion pairs such as butyl lithium (BuLi), and their degree of association under equilibrium conditions.

Polybutadiene and polyisoprene with terminal hydroxyl groups at each end of the molecule have been prepared by polymerization of the appropriate monomer with lithium complexed with naphthalene or other polycenes, followed by reaction with ethylene oxide or carbonyl compounds[141].

A new laboratory device for continuous measurement, by monomer contraction, of the polymerization rate of isoprene in the presence of lithium has been described[144].

The two major types of catalysts under consideration are lithium or organolithium compounds, and the Ziegler-type catalysts.

Specificity of catalytic effect is illustrated by the fact that a Ziegler-type catalyst of aluminum alkyl and titanium tetrachloride seems to be preferred for *cis*-1,4-polyisoprene, and a catalyst of aluminum alkyl and titanium tetraiodide for *cis*-1,4-polybutadiene. The ratio of components in the Ziegler-type catalyst to a great extent, and temperature and pressure of reaction to a lesser extent are other factors which determine the type of polymer obtained.

There are small but definite differences in structure between polyisoprenes prepared with Ziegler-type and lithium-containing catalysts. Infrared absorption measurements indicate the former type to have about 95% *cis*-1,4-content, whereas the latter is about 93%. Lithium rubbers crystallize slowly or not at all at −25° C; Ziegler-type rubbers require about 25–50 hours, or considerably longer than required by natural rubber.

In terms of molecular weight, the lithium-catalyzed rubbers have very high values, higher than natural rubber, and therefore require substantial mastication for satisfactory processing. Lithium derivatives, such as butyl lithium, probably offer more latitude in control of molecular weight. Ziegler-type catalysts will produce polymers in a lower molecular-weight range, up to the molecular weight of hevea.

These factors account for some of the differences in properties found with these polymers. Since the Ziegler-catalyzed polyisoprene is easier to crystallize, it has better hot tensile strength. The higher molecular weight range of the lithium-catalyzed polymer, on the other hand, favors high resilience and less heat generation.

The physical characteristics of polyisoprenes with *cis*-1,4-contents in the range 89–98% were studied[155]. While these differences in micro-structure did not appear to have much effect on viscoelastic properties such as internal friction, resilience and stiffening temperature, other characteristics, such as rate of crystallization and gum tensile strength, were definitely influenced adversely by structural imperfections in these stereo rubbers.

The properties of the various isoprene rubbers, especially Coral rubber, Ameripol, and SKI, have been tabulated and compared with those of SBR cold rubber and *cis*-1,4-polybutadiene[64]. Natural rubber contains about 98% of the *cis*-1,4 structure and 2% of the 3,4-addition structure, whereas the synthetic types contain 90–95% of *cis*-1,4 structure and 3–7% of the 3,4-addition structure, plus in some cases a small amount of the 1,2-addition structure. There are in natural rubber appreciable amounts of non-rubber components, such as antioxidants, proteins, fatty acids, which are absent from the synthetic products. These deficiencies can be made up by the addition of antioxidants and other compounds which help to stabilize the polymer and cause it to behave, in processing characteristics and cure rate, more nearly like the natural product.

The gum tensile strengths of the synthetic products usually are in the range of 2500 to 3500 psi, as compared to 3000 to 4000 psi for natural rubber and only 200 to 300 psi for SBR. However, the Russians have reported a value as high as 4200 psi for a gum vulcanizate of SKI. The synthetics exhibit a greater elongation at break (800 to 1000 psi) than natural rubber or SBR (700 to 800 psi). The 600% modulus values are 700 to 1200 psi for natural rubber, 300 to 800 for the synthetic isoprene rubbers, and only 50 to 150 for SBR. The isoprene rubbers process well and are easily compounded. They are usually of lower molecular weight than natural rubber and do not require premastication.

In carbon-black-reinforced vulcanizates, the relatively small differences just noted tend to disappear. The tensile strength and ultimate elongation values of natural rubber, polyisoprene, and SBR are equivalent. The normal and hot tensile strengths of *cis*-polyisoprene are comparable to those of natural rubber.

Truck tire tests have been made with synthetic polyisoprene substituted in place of natural rubber. In some cases the synthetic tires have exhibited better tread crack resistance than natural rubber. Tread wear usually is in the range of 85–95% of that obtained with natural rubber. Thus the synthetic polymers are quite often somewhat inferior to the natural product, but the small gap is expected to be closed with better control over such factors as the *cis*-1,4-content and molecular weight distribution in the synthetic polymers.

Reports have been issued on actual tire tests with heavy duty tires for trucks, buses and airplanes, and show that with respect to wear and heat build-up the isoprene rubbers are comparable to natural rubber during tire operation[2, 18, 24, 81, 98, 157]. High-speed jet aircraft tires made entirely of polyisoprene rubber and capable of withstanding landing speeds as high as 250 mph passed rigid durability tests that qualified this synthetic rubber for jet aircraft service[24]. The tires also successfully withstood temperatures in excess of 250° F, which corresponds to the almost instantaneous heat build-up generated by high-speed landings.

2. *Deuterio rubber.*—An interesting variation in the synthesis of natural rubber is deuterio rubber[156, 158]. The first problem was to synthesize the monomer perdeuterio isoprene from acetone-d_6 and acetylene-d_2[70]. The intermediate, 3-methyl-butyne-1-ol-3-d_8, was obtained, partially reduced with deuterium and dehydrated to isoprene-d_8. The monomer polymerized in the presence of a Ziegler catalyst prepared from titanium tetrachloride and tri-

isobutyl aluminum. It polymerized faster and yielded a polymer of higher molecular weight than did isoprene under comparable conditions.

The x-ray diffraction pattern of the new rubber was identical with that of natural rubber and *cis*-1,4-polyisoprene. The evidence strongly indicates that not only does deuterio rubber have the same *cis*-1,4 head-to-tail structure of natural rubber, but also the same crystalline structure and the same dimensions in the unit cell.

Deuterio rubber is not a commercial possibility because of the high cost of deuterium and of the monomer isoprene-d_8. However, the rubber has many interesting properties and some may be superior to those of natural rubber. Further work is justified in this area since the extension of our scientific knowledge about isoprene elastomers may ultimately lead to a polymer superior to natural rubber.

3. *Polybutadiene.*—Work on the duplication of natural rubber has stimulated interest in stereo-regulated polymerizations with related monomers such as butadiene. In April 1956, Phillips Petroleum stated that its scientists had successfully prepared a *cis*-1,4-polybutadiene rubber which generates less heat than styrene rubber and approaches natural rubber in this respect[8]. A typical Phillips sample exhibits the following composition: 94.5% *cis*-1,4; 1.8% *trans*-1,4; and 3.7% 1,2-addition content. Procedures have since been worked out for the preparation of a wide variety of linear polybutadienes containing both *cis*- and *trans*- configurations, as well as 1,2- and 1,4- addition types. Although polybutadiene cannot be classified as a synthetic natural rubber type since its composition is different from that of hevea, it can be substituted for natural rubber in varying amounts according to the intended end use[17, 29, 34, 72, 88, 109, 148, 149, 150, 151, 152, 159, 160, 172]. Phillips Petroleum has continued with the development of this rubber under the trade mark "Cis-4"[33], and with "Trans-4", a polybutadiene of about 90% *trans*-1,4 content which in physical properties resembles balata and gutta percha[45]. Butadiene polymers prepared with organosodium catalysts have also been described[119, 120].

When butadiene is polymerized with stereospecific catalysts, a hydrocarbon solvent is normally employed which is recovered and recycled after polymerization. Recent work at Chemische Werke Hüls in Germany has been carried out in the absence of a solvent[85]. Butadiene is continuously bulk polymerized in the presence of a Ziegler type catalyst dissolved in an extender oil, which results in a product that is oil-extended to a moderate degree. Monomer and catalyst are fed into a polymerization chamber and the elastomer is extruded as it is formed.

By proper control of the stereospecific catalyst and polymerization conditions, the *cis*- and *trans*-contents of 1,4-polybutadiene can be varied over a wide range, from over 95% *cis*- to nearly 100% *trans*-configuration. A catalyst derived from an aluminum alkyl and titanium tetraiodide is generally favored for formation of a polymer with high *cis*-content. If the polymer contains at least 15% *cis*-content, the vulcanizate is completely rubbery at ordinary temperatures[150]. With a *trans*-content of 93%, the vulcanizate is tough, leathery, and crystalline at 80° F. Important physical properties appear to change little in the range of 25% to 80% *cis*-content. Typical properties of the vulcanizates include low gum tensile strength, high tensile strength in black loaded stocks, excellent resilience even at −40° F, and low brittle point. A polymer with moderate *cis*-content (82–87%) exhibits very little tendency to crystallize at low temperatures, hence is completely rubbery down to the brittle point of −85° C. A polymer with 80% *cis*-content exhibited a Gehman freeze point of −97° C[148].

Polybutadienes of varying structure were obtained by Natta and co-workers depending on the catalyst and conditions employed for their preparation[93, 129]. If the catalyst was a soluble complex of aluminum triethyl and vanadium triacetylacetonate, crystalline 1,2-polybutadienes with syndiotactic structure were obtained, admixed with amorphous polymers with 70–80% 1,2-addition content[131].

Another structural characteristic having an important bearing on properties is the *cis*-content of 1,4-polybutadienes. Natta has prepared polymers of varying *cis*-content and compared the properties of their gum vulcanizates[132]:

Cis-1,4 content	88–90%	96–98%
ML-4 (raw polymer)	90–95	70–80
Tensile strength, psi	800–1100	2500–2800
Elongation, %	900–1000	850–950
300% modulus, psi	140–180	140–180
Resilience @ 20° C, %	80–85	85–88
Shore A hardness	45–50	45–50

The polymer of very high *cis*-content is definitely superior from the standpoint of gum tensile strength and resilience. A crystalline polybutadiene with mainly *trans*-1,4 structure and high melting point (140–145° C) can also be obtained if the catalyst composition is changed[127].

Montecatini employs a soluble cobalt catalyst to produce on a pilot plant scale a polybutadiene with the following properties[139]: *cis*-1,4-content greater than 97%; melting point *ca.* 1° C; Mooney viscosity (ML-4) of 45; intrinsic viscosity of 2.4 to 2.8; and weight to number average molecular weight ratio of 2.5.

Natta and Corradini[134, 135] have made a thorough study of the structure of crystalline hydrocarbon polymers, including the various possible forms of polybutadiene (*cis*-1,4; *trans*-1,4; 1,2-isotactic; 1,2-syndiotactic). The *cis*-1,4 form exhibits a melting point of about +1° C and is the only one with rubbery characteristics at room temperature. The other three forms are crystalline solids of possible use as plastics and fibers.

Polybutadiene of intermediate *cis*- and *trans*- content is obtained by polymerization of the monomer with butyl lithium initiation in *n*-heptane[102]. The structure of a typical polymer was analyzed by several infrared procedures and found to be as follows: 48–58% *trans*-1,4-; 33–45% *cis*-1,4-; and 7–10% 1,2-addition (values depend on infrared procedure employed). Other infrared studies of polybutadienes prepared with stereospecific catalysts have been reported[116]. The catalyst requirement and kinetics of butadiene polymerization in the presence of lithium are reported[142].

The crystallization in the unstretched state of a polybutadiene sample with a high *cis*-content was studied[172]. Peroxide-cured samples crystallized more slowly when measured at a fixed temperature, but even fairly tightly cured polymers crystallized readily. Isomerization of a portion of the *cis*-structure to the *trans*-structure also resulted in a decrease in the rate of crystallization, but this may be accounted for by the depressed melting point of the modified samples[173].

Bulgin reported that 96% *cis*-1,4-polybutadiene mills satisfactorily only over a narrow temperature range (50 ± 2° C)[67]. If 10 phr of light mineral oil is added, the temperature range for smooth banding on the mill is increased to 35–50° C. The ability to band smoothly seems to depend upon the amount of stretch in the rubber, in that the rubbers which banded smoothly had high

300% modulus values. The *cis*-content of the polymer also affected the critical mill temperature:

Cis content, %	Critical mill temperature, ° C
97	53
96	50
91	35

The critical mill temperature is increased about 10° for carbon black compounds.

cis-Polybutadiene blends readily with natural rubber and the blends have shown excellent physical properties[149]. A 1:1 blend displayed hysteresis properties equivalent to the natural rubber control and exhibited satisfactory modulus, tensile strength and hardness. Tests on retreaded passenger tires gave outstanding abrasion resistance and increased resistance to cracking as compared to natural rubber. The compatibility and good processing characteristics of the blends have been confirmed by factory mixing trials.

Service tests have shown *cis*-polybutadiene treads in passenger car tires to give an average of 36% better wear than SBR 1500[151]. If it was blended with an equal amount of natural rubber, 10 to 15% better tread wear than with natural rubber was obtained in year-round tests with passenger car and truck tires.

Additional tests of *cis*-polybutadiene and blends with natural rubber in tire treads have given the following results[74]:

Tire type	Passenger	Passenger	Truck
Experimental stock	*Cis*-4	50/50 *Cis*-4/hevea	Blends of *Cis*-4/hevea
Control stock	SBR 1500	hevea	hevea
Tire miles in test	570,000	254,000	2,000,000
Tread wear rating	126	116	114

Interest in *cis*-polybutadiene has also been evidenced by other rubber companies. Firestone has announced work on Diene rubber, a polybutadiene of intermediate *cis*-content which is made with an alkyl lithium catalyst[3, 10, 16, 161]. Diene rubber is claimed to be at least equal to natural rubber in resilience, hysteresis loss, and low temperature properties. Tire treads are improved in wear resistance, cracking resistance, and other important properties when Diene rubber is used in a 50/50 blend with SBR for passenger tires, and with natural rubber for truck tires. Goodrich-Gulf Chemicals has announced work on, and eventual commercialization of, a polybutadiene (Ameripol CB) of undisclosed composition[42]. Goodyear has announced plans for the production of a polybutadiene rubber, Budene, and Natsyn at a new plant site near Beaumont, Texas[51]. Other American producers of stereo rubbers will be American Rubber & Chemical, Shell, and Texas-U. S. Chemical. Chemische Werke Hüls plans to produce in Germany a polymer with the following characteristics: 98% *cis*-1,4 content, molecular weight of 430,000, intrinsic viscosity of 2.5, and a rather broad molecular weight distribution[35].

Since butadiene of high purity is available in commercial quantities, and *cis*-polybutadiene seems to have real merit as a tire rubber, large scale production of this new rubber can be readily visualized. The commercialization of both *cis*-1,4-polyisoprene and *cis*-1,4-polybutadiene is expected to proceed at a very rapid rate so that by the end of 1962 U.S.A. production capacity will exceed 200,000 long tons annually[47, 52].

4. *Other polydienes.*—Although butadiene and isoprene are by far the most important dienes in the elastomer field, several others have been the subject of recent research investigations.

A Russian research study was made of the polymerization of higher diene hydrocarbons[107]. Polymers were prepared, with lithium or a butyl lithium catalyst, from 2-ethyl-1,3-butadiene; 2-isopropyl-1,3-butadiene; and 2-methyl-1,3-pentadiene, as well as isoprene. Rapid polymerization rates were obtained with all monomers except methylpentadiene. The physical properties were listed as follows:

			Properties of gum vulcanizates		
Polymer	Plasticity	Vitrification temperature, °C	Strength, psi	Elong., %	Permanent set, %
Polyisoprene	0.35	−68	3300	1180	14
Polyethylbutadiene	0.56	−76	2800	1220	14
Polyisopropylbutadiene	0.36	−52	1625	1080	16
Polymethylpentadiene	0.66	−28	2800	620	14

It will be noted that good gum tensile properties were obtained in all cases. The brittle point was fairly high in the case of the methylpentadiene polymer and unusually low for the ethylbutadiene polymer. Russian work was also reported on the polymerization of piperylene (1,3-pentadiene) to elastomers resembling sodium butadiene rubber in properties[105], and on the copolymerization of isoprene with piperylene and 2,3-dimethyl-1,3-butadiene[146].

Copolymers of butadiene and methylpentadiene were studied over a wide range of monomer ratios[162]. Methylpentadiene normally consists of a mixture of 85% 2-methyl-1,3-pentadiene and 15% 4-methyl-1,3-pentadiene. The copolymers were prepared by emulsion polymerization at 50° C, and the swelling behavior and low temperature properties of their vulcanizates were measured. Maximum swelling, in a test solvent consisting of 70% isooctane and 30% toluene, occurred in the stock of copolymers containing 20–30% butadiene. The freezing temperature of the copolymer decreased regularly with increasing butadiene content. It was concluded that a 50/50 copolymer had the best balance of properties and would be most useful as a synthetic sealant for self-sealing fuel tanks.

A *cis*-1,4 polymer of 2,3-dimethyl-1,3-butadiene has been prepared by use of a Ziegler type catalyst[180]. This polymer, however, is a plastic with m.p. 189–198°, intrinsic viscosity 0.6–0.9, and fiber repeat distance of 7.0 A. Infrared absorption and x-ray diffraction data led to the conclusion that the polymer had a *cis*-1,4 structure. A *trans*- form of still higher melting point (260–263°) was prepared by use of the canal complex polymerization technique[65]. The *trans*-1,4 form can also be prepared with an aluminum triisobutyl-titanium tetrachloride catalyst if an Al to Ti mole ratio of 0.25 is employed[181].

Liquid butadiene-styrene copolymers can be prepared in a hydrocarbon diluent in the presence of an alkali metal catalyst, usually sodium or potassium. Oxygenated compounds, such as dioxane or ether, are used in small amounts to improve the polymerization rate. These new materials are being commercialized as Buton resins by Enjay Chemical's plastics and resins division. As a new class of thermosetting resins, they will be employed in surface coatings for appliances, home furnishings, industrial items, and for automotive primers[48].

A highly crystalline polymer of 80 to 95% *cis*-1,4- configuration is obtained by polymerization of 2-phenyl-1,3-butadiene with a Ziegler catalyst such as triisobutyl aluminum-titanium tetrachloride[164].

III. OLEFIN POLYMERS AND COPOLYMERS

Considerable interest was aroused by Montecatini's announcement of a new ethylene-propylene copolymer elastomer, C 23, in semicommercial production at its plant in Ferrara, Italy[9, 11, 27, 30, 36, 40, 41, 114]. A Pirelli 5:20-12 passenger car tire with a C 23 tread was exhibited in Milan which showed little wear after 10,000 miles use. This development was based on research studies by Natta and coworkers of the polymerization of olefins and mixtures of olefins with stereospecific catalysts, which are covered in a series of papers[110, 111, 115, 122, 123, 124, 125, 126, 128, 130, 133, 136, 137, 138, 140]. Technological evaluation of these copolymers in the Pirelli laboratories has been reported[68]. The development is of keen commercial interest since the raw materials are the cheapest ones known for the production of an elastomer.

The copolymers desirable for use as elastomers are amorphous in nature and can vary in ethylene/propylene ratio over a wide range, from about 35 to 65% of either monomer contained in the product. One of the chief problems in their preparation is the fact that ethylene polymerizes may times faster than propylene, so that the formation of random copolymers is difficult to achieve. It is more likely that these copolymers are of the block type.

In one of the studies[111], the catalyst employed was a complex of vanadium tetrachloride and trihexylaluminum. The copolymers exhibit solubilities which differ from those of the homopolymers, have a characteristic infrared spectrum, and possess an amorphous nature as evidenced by their x-ray diffraction patterns. Other catalysts described are made from vanadium oxychloride and aluminum alkyls, from vanadium trichloride and aluminum alkyls[124], as well as as from trihexyl-aluminum and titanium di-, tri-, and tetra-chlorides[125]. Values of the reactivity ratios of the two monomers in the copolymerization reaction were determined and found to vary over a wide range.

Copolymers of ethylene and propylene over a wide range of composition and molecular weight were prepared by Amberg and Robinson[4]. Good elastomeric properties were obtained with copolymers containing 60 to 70 mole per cent ethylene, reduced specific viscosities of 3 to 4 (0.1% in decalin at 275° F) and Mooney viscosities (ML-4, 212° F) of 30 to 45. The monomer distribution in the polymer chain is essentially random. Thus there are occasional runs of the same monomer, but few segments of block polymer. The copolymers show little crystallinity and are considered to have a linear structure, with very little chain branching and residual unsaturation. Best properties appear to result from narrow molecular weight distribution and high uniformity of composition.

The viscoelastic properties of E/P copolymers were studied in considerable detail and found quite different from those of crystalline polymers or mechanical mixtures of the homopolymers[128]. The dynamic properties are good even at low temperatures, as evidenced by the fact that the minimum impact resilience (for polymers containing more than 45% ethylene) was at a temperature of less than −40° C. The flexibility of the molecule increases with increase in the ethylene content, and is accompanied by a lowering of the temperature of minimum elasticity.

In a study of dynamic mechanical properties of new elastomers, E/P copolymers (60/40 and 50/50 mole %) resembled SBR in power loss, modulus, and related properties. They exhibit a second transition temperature around 50° C, which is attributed to ethylene block crystallinity, and it is not known what effect this will have in dynamic applications[77].

Montecatini, in its announcement of C 23 ethylene-propylene elastomer, revealed technical data on its physical properties. The fact that the molecule is practically free of double bonds is responsible for outstanding resistance to heat, oxygen, ozone and other aging and degrading agents. Wear properties are also stated to be excellent. On the other hand, the saturated nature of this elastomer precludes the use of conventional sulfur-accelerator systems, and it is necessary to employ another technique of crosslinking, such as with peroxides. The effect of crosslinking density on physical properties has been studied[71].

The rebound value (Luepke pendulum) at 20° C is 75% and the minimum value occurs at −35° C. The brittle point is well below that of natural rubber. The specific gravity is unusually low for an elastomer—0.85 to 0.86. Permeability to gases is very similar to that of natural rubber.

It is also claimed that the new elastomer can be easily mixed with normal fillers, and that C 23 stocks can be satisfactorily processed with equipment and techniques standard in the rubber industry. Mechanical properties of vulcanizates are generally intermediate between those of natural rubber and SBR, as shown in this tabulation:

Mechanical Properties	C 23	NR	SBR
Tensile strength, psi	3600–4000	4100–4400	3700–3900
Elongation at break, %	450– 500	550– 600	400– 450
300% modulus, psi	1300–1700	1600–1700	1650–1900
Tension set, % (after 200% elongation)	7– 9	6	9
Hardness, Shore A	60–65	65	67

Stocks contained 50 phr HAF Black

Much work has been done on the polymerization of other olefins and mixtures of olefins with sterospecific catalysts, but since the resulting polymers are likely to be plastics rather than elastomers, they will not be discussed in detail in this review. Polybutene-1 exhibits outstanding resistance to stress cracking, good cold flow characteristics, and high burst and tear strengths, so its major applications are probably for film and pipe[44]. Examples of copolymers are those made with ethylene and 1-butene[145], and propylene and 1-butene[112].

IV. BUTYL RUBBER DEVELOPMENTS

Butyl rubber is increasing in importance, as evidenced by the announcement of Standard Oil of New Jersey to increase the capacity of its plants by 38,000 long tons/year to a total of 156,000 long tons/year. The widespread introduction of the tubeless tire in 1954–55 temporarily reduced the consumption of butyl rubber, but the future is considerably brighter because of the development of chemical modifications of butyl, the all-butyl automobile tire[86], and the continued substantial production of butyl tubes for passenger, truck and bus tires.

Halogen treatment of butyl results in modifications which could substantially increase the total usage of butyl. The chlorination (with chlorine or sulfuryl chloride) of butyl rubber to a chlorine content of 1% or more produces an elastomer with much broader utility[82, 83, 87]. In chlorobutyl (MD-551) the chlorine atom is believed to promote an interaction between polymer and carbon black, which permits lower processing temperatures and less mixing time for attainment of optimum physical properties. Adhesion to, and compatibility with, natural rubber, neoprene, nitrile rubber, or SBR are also in-

creased. Vulcanization may be accomplished with magnesium oxide[75], zinc oxide alone or zinc oxide-thiuram blends, or with a phenol-formaldehyde resin. The cured compounds are characterized by low compression set, and excellent resistance to flexing, abrasion, and the effects of oxygen and ozone. Chlorobutyl is recommended as a tire inner liner because of its airholding and age-resisting properties, and its good adhesion to a natural rubber carcass stock[89].

Other halogen treatments of butyl have been described[117, 118]. The bromination of butyl to a bromine content of 1.0–3.5% has been found to increase the cure rate without harmful effect on other properties. Other advantages found are improved compatibility with natural and synthetic rubbers, and increased adhesion to other rubbers and metals. Iodine monochloride and iodine monobromide modify butyl in much the same manner as bromine alone. It is postulated that during vulcanization the small amount of iodine remaining in the polymer enters into the vulcanization reaction with the metal oxide, and thus accounts for the better compatibility with natural rubber and for the improved adhesion.

It has been reported that these halogen-modified butyl rubbers exhibit less power loss and higher resilience at a given temperature than the commercial grades of butyl[77].

The vulcanization of butyl rubber with modified phenolic resins and a halogen-containing activator (i.e., resin-cured butyl) has become of commercial importance because it provides vulcanizates of greatly improved heat and oxygen resistance[168]. Typical examples are 2,6-dimethylol-2-hydrocarbylphenols or their condensation polymers. The activator may be stannous chloride, neoprene, or Hypalon. A typical commercial resin is ST 137 (Rohm & Haas). Curing bladders exhibit a much longer useful life when cured in this manner rather than by the usual sulfur cure. For example, a resin-cured butyl stock can be heated for 16 hours at 322° F without the occurrence of reversion. It is assumed that crosslinking occurs through the double bonds in the butyl molecule, since the unsaturation disappears during the vulcanization.

Butyl rubber and carbon black apparently form complexes by chemical or physical processes which result in enhanced properties in the vulcanizate[84]. The reaction occurs during mixing and is increased by the action of heat and chemical promoters.

The abrasion resistance of butyl tread stocks was studied in a series of statistically designed experiments[182]. Of the variables studied, reduction in sulfur content of the formulation offered the most significant improvement in abrasion resistance.

In 1959 Esso Standard Oil began to market through its sales affiliate, Enjay, an all-butyl passenger tire under the Atlas Bucron label[32, 40]. The company has tested the tire extensively and has claimed a number of advantages over the conventional tire, such as smoother ride, no squealing or screeching when cornering, quicker stopping, and greater resistance to ozone. A "quiet-ride" tire of similar characteristics but different composition has been announced under the name Plioprene (Goodyear)[25].

One of the major factors in making the butyl tire possible was the development of a butyl "latex" (made by dispersing butyl rubber in water) which was employed to increase the bonding strength between fabric and rubber in the carcass of the tire. The Department of the Army has also approved the use of butyl tires for certain military uses. Additional time will be required before one can assess the full impact of the butyl tire on the highly competitive tire market.

Butyl rubber is available in the form of an anionically emulsified high solids latex and its properties and applications are described[113].

V. RUSSIAN SYNTHETIC RUBBERS

On the basis of available information, Russian technology in the field of synthetic rubber is well advanced[5, 59, 177]. Reference has already been made to a number of fields in which research and development investigations have been undertaken. The following types of synthetic rubber are stated to have reached the commerical stage in Russia: sodium- and potassium-catalyzed polybutadiene, butadiene-styrene copolymers (solid rubber, oil-extended, and latex types), butadiene-α-methylstyrene copolymer, butadiene-acrylonitrile copolymers, butadiene-vinylpyridine copolymers, polypiperylene, polychloroprene, butyl rubber and polyisobutylene, silicone rubbers, and *cis*-1,4-polyisoprene. In comparison with the American situation, a major difference is the emphasis on sodium butadiene rubbers, which at the beginning of 1959 constituted about one-half of their entire synthetic rubber production. Much of the future expansion in production, however, is expected to occur in emulsion-type butadiene-styrene rubbers similar to our SBR, as well as in *cis*-polyisoprene. Some of the rubbers stated to be in commercial production in Russia, such as polypiperylene and butadiene-α-methylstyrene copolymer, have also been investigated in this country but were not of sufficient interest to be commercialized.

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THE CHEMISTRY OF NATURAL RUBBER PRODUCTION *

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Many advances in the world of science have taken place quietly in field and laboratory, with few to applaud the discoverer or to appreciate his worth. The man we honor today was such a pioneer, whose work received full recognition only many years after its completion. It is, I think you will agree, a very fitting tribute to Ridley to discuss recent advances in the science of natural rubber and to applaud at least some of the contributions made by the many different workers.

The field is a large one, and I can hope only to give a brief survey of a few selected items, so I propose paying more attention to research which is concerned with the production of natural rubber rather than with its utilization.

LATEX PARTICLES

The raw material of the rubber industry is latex from *Hevea brasiliensis*, which has long been known to consist of a colloidal suspension of rubber particles in serum. As well as rubber particles, the presence of yellow lipid globules was recognized by Frey-Wyssling[1] in 1929 and are now known as *Frey-Wyssling particles;* aggregates of another type of nonrubber particle were described by Homans and van Gils[2, 3] in 1948. The latter were named *lutoids* and can be separated by centrifugation.

In 1953 the effect of high speed centrifuging (to give 59,000 *g*) on latex was described by Cook and Sekhar[4]; they observed separation of field latex into four fractions, described as a top layer of cream, a yellow-orange layer below it, a bottom layer of rather gelatinous material, and a layer above it of clear serum. Following up this observation, Moir[5] showed in 1959 that by collecting latex from the tree in vessels surrounded by ice and continuing all operations under

* Text of a lecture given at Akron University November 18, 1960, to the Rubber Science Hall of Fame Meeting.

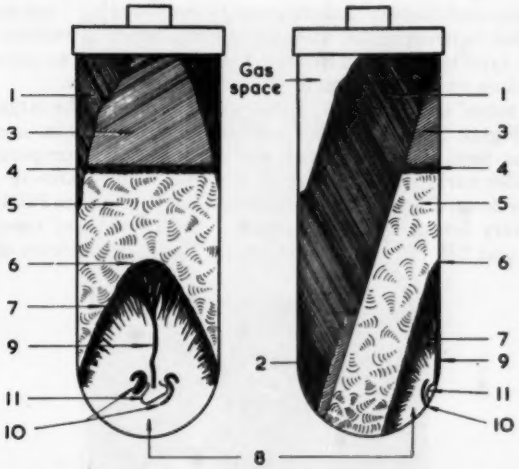


FIG. 1.—Diagram showing different zones obtained by high-speed centrifuging of fresh latex from *Hevea brasiliensis* under refrigeration conditions (Moir[5]).

refrigerated conditions so that the temperature never rose above about 5° C eleven separate zones could be distinguished after centrifugation in a Spinco model L centrifuge, at 53,000 *g* max. Some of these zones can be colored by using vital stains and are then more readily identified. A diagram showing the zones according to Moir is given in Figure 1.

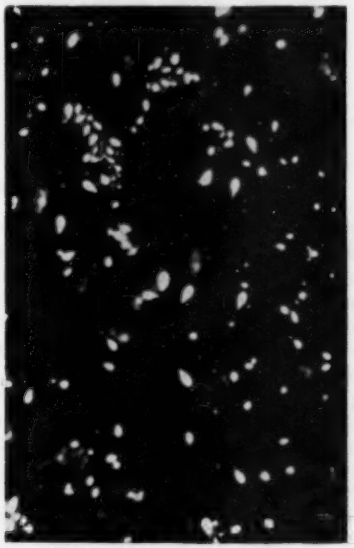


FIG. 2.—Pear-shaped particles[6] in hevea latex (×1600).

Microscopic examination of these zones by Southorn[6, 7, 8] has revealed them to be somewhat heterogeneous, each being composed of a variety of particles, although one type may predominate. The study has led to some interesting new observations on the constituent particles of fresh latex.

The upper zones[8] contain most of the rubber particles, the larger ones being at the top (Figure 2). Large and medium shaped particles are often pear-shaped as has been described much earlier[9, 10, 11]. The proportion of pear-shaped particles varies with the age of the tree, being scarce in young trees. There are also clonal differences; for example trees from clones PB 84 and RRIM 526 showed very few pear-shaped particles even in matured trees, whereas in clones Tjir 1 and PR 107 a high proportion of pear-shapes were distinguished.

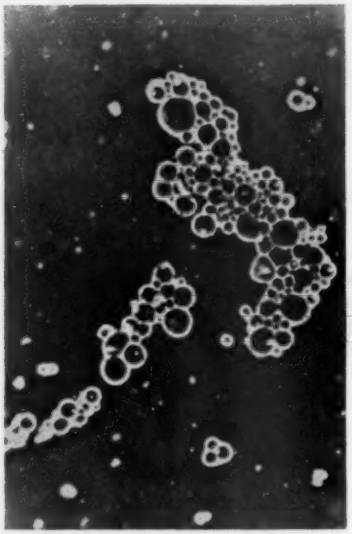


FIG. 3.—Cluster of lutoids (×1600).

The pear-shaped particles are typically 2 to 4μ long and half as broad. Occasional particles with very long tails, as much as 10μ, have been observed; in most cases the tails were parallel sided, but a few showed swellings at intervals. Very small rubber particles are difficult to identify, particularly so since in fresh latex rubber particles are difficult to stain.

The lutoids[8], which are found largely in the bottom fraction after centrifuging, appear as spheres, 2 to 10μ diameter, bounded by a definite membrane (Figure 3). Moving inside are many smaller particles[8] in vigorous Brownian movement (Figure 4). After tapping, the lutoids undergo degeneration; the interior movement stops and the particles adhere to the membrane. Later the membrane breaks down. Hsia showed that repeated freezing and thawing of the bottom fraction which consists largely of lutoids, yields a liquid which is probably the fluid contents of the lutoid bodies[12]. Treatment of the bottom fraction by ultrasonic vibration has a similar effect[9a]. The mobile colorless liquid obtained has a slightly higher density than that of the normal serum

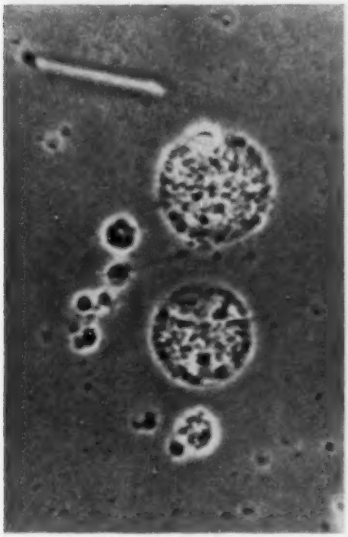


FIG. 4.—Separate lutoid[8] bodies, showing interior particles (×2000).

separated from latex by high speed centrifuging. It is interesting to record that after resting the tree for some time, the lutoids found in the latex on first tapping are small, and so tightly packed with inner particles that Brownian motion is greatly hampered. The inside particles are larger than those shown by a tree in regular tapping.

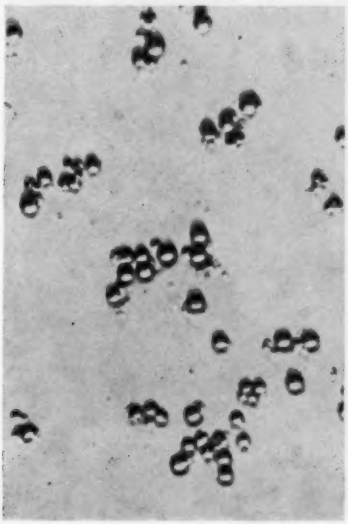


FIG. 5.—Frey-Wyssling particles[8] (×1024).

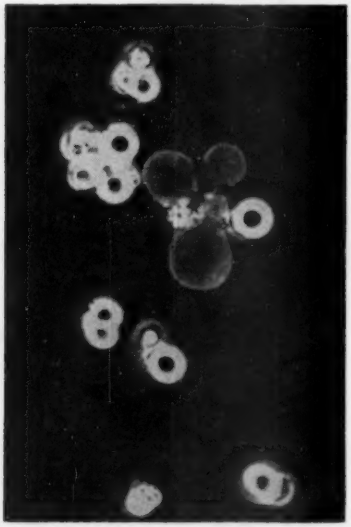


FIG. 6.—Grey vacuolar bodies[8] with Frey-Wyssling particles (×1600).

The yellow particles[8] described by Frey-Wyssling[1] occur in the upper zones as well as the lower and their densities must therefore show a considerable range in value (Figure 5). They are usually spheres of about 2μ diameter ranging in color from reddish brown through bright yellow to almost colorless. Some stain with osmic acid and some do not. They often occur in clusters.

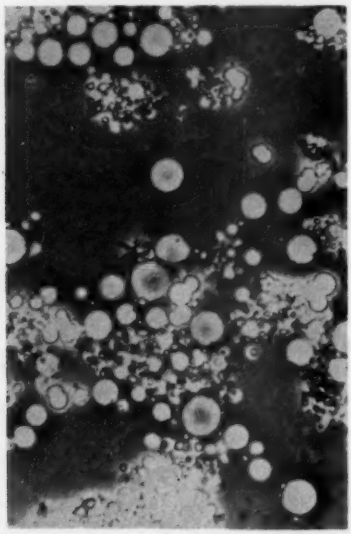


FIG. 7.—Pale grey lutoids, almost black under anoptral phase[8] contrast (×1024).

FIG. 8.—Opaque, notched particles[8] (×2000).

Three new types of spherical particles[8] were also observed. A grey vacuolar body sometimes very large, is often found associated with Frey-Wyssling particles (Figure 6). The second new type comprises freely moving spheres 2 to 10μ in diameter, which appear pale grey under positive phase contrast and

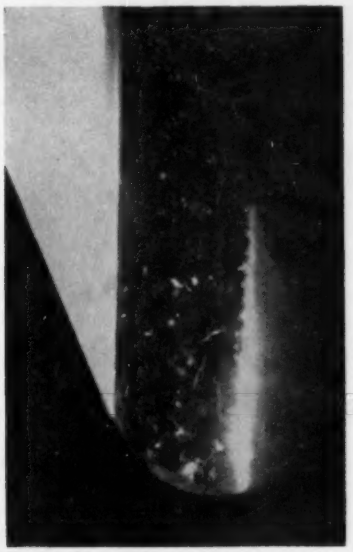


FIG. 9.—Centrifuged latex showing "ropey" texture[8] of serum layer (×2).

FIG. 10.—"Ropey" material from Figure 9 at higher magnification showing bunched particles[9], (×1650).

almost black under anoptral phase (Figure 7). Sometimes smaller particles are observed in active movement inside these spheres. The third type of particle consists of grey solid opaque spheres, 1 to 5μ in diameter (Figure 8). The periphery sometimes shows notches, as though solid spheres have been

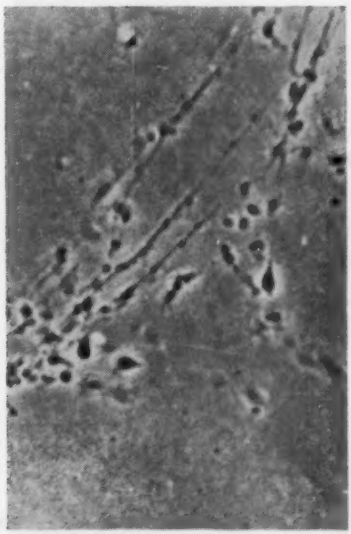


FIG. 11.—Threads[9] with particles attached (×2000).

squashed to fracture; further notches can be created by deliberate compression. These spheres are usually associated with the heavier Frey-Wyssling particles in the bottom fractions separated by high speed centrifuging.

A further new series of structures[3] have also been observed; these consist of long fine threads and may be of fundamental importance. They are found in most of the fractions separated by high speed centrifuging but are most prevalent in the serum fraction to which they give a "ropey" appearance (Figure 9). These structures consist of tangles of threads (Figure 10) to which are attached pear-shaped rubber particles by the narrow end (Figure 11), Frey-Wyssling particles in clusters, lutoids and innumerable much smaller particles which have not yet been identified; the whole appears embedded in a transparent, jellylike matrix. It is thought that these aggregates may be part of a cytoplasmic structure in latex cells carried away with the flow of latex when the tree is tapped.

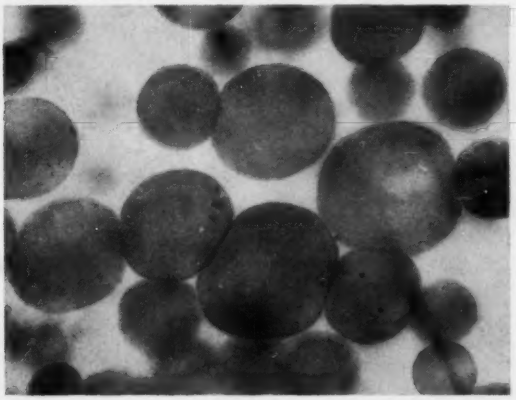


FIG. 12.—Ultra thin section[12] of latex rubber particles under electron microscope.

The threads themselves form an interesting study since they sometimes undergo changes after removal from the tree. In some cases detached threads have been observed studded at intervals with small particles. The thread thickens considerably over a period of a few hours, developing local swellings within which small particles showing Brownian movement can be seen. The threads thus appear to be very fine tubes. Further evidence for this comes from an examination of lutoids to which threads are attached. In these cases the thread has been observed to thicken and swell after which the lutoid discharged part of its contents into the "thread", the whole system then appearing like an elongated lutoid.

It thus seems very likely that the threads observed form part of a reticulum of hollow threadlike structures within the latex vessels, to which the different latex particles may be attached. Such a cytoplasmic membrane system or parts of it could well provide a site for biogenesis, and recalls the endoplasmic reticulum described first in animal cells (Porter[13], Palade[14], Robertson[15]) and later demonstrated in plant cells (Hodge et al.[16], Mollenhauer[17]), although this reticulum is usually regarded as submicroscopic.

The suggestion that latex may be considered as diluted whole cytoplasm was suggested as long ago as 1886 by Berthold[18] and later by Milanez[19]. Fur-

ther support for this view comes from recent work in England carried out by Andrews and Dickenson[20] using young rubber trees grown in a hothouse, in which thin sections of laticiferous tissue were studied by an electron microscope. Latex in the vessels appears bounded by a thin membrane closely opposed to the vessel wall. The contents of the vessel are heterogeneous, comprising rubber and larger particles with a diffuse structure. Although these workers make no reference to nuclei, it has of course long been known that they are present in latex vessels[21].

Ultrathin sections of rubber particles[20] in fresh latex from the young trees showed a spherical shape, (Figure 12), but there was no evidence of aggregation of small particles to form larger ones, as has been proposed by workers in Indonesia[22, 23]. The interior of the particles shows a homogeneous structure in respect of electron density, but at the periphery is a boundary layer which may be double.

BACTERIA IN THE TREE AND IN LATEX

As may be anticipated from its biological source, rubber latex is an exceedingly complex system, and contains a variety of nonrubber constituents. For example recent studies on proteins by Karunakaran, Moir and Tata[25] using starch gel electrophoresis have demonstrated twenty two different components in the serum fraction and ten components in the bottom fraction separated by high speed centrifuging, only one of which appears to occur in the serum fraction, the remainder appearing to be different[24, 25]. A number of carbohydrates and lipids are also present[26]. This plenitude of organic substances and the presence of mineral elements as well, renders rubber latex particularly prone to attack by bacteria. The fact that latex quickly putrefies after collecting from the tree soon earned a reputation for the obnoxious odor developed. Steps were taken to avoid putrefaction, by adding suitable anticoagulants or preservatives such as sodium sulfite, formaldehyde or ammonia. It is however, only during recent years that a systematic survey was carried out by Taysum[27] to identify the bacteria responsible for these putrefactive changes in latex. This work resulted in the isolation of nearly 100 different species of bacteria from field latex and ammoniated latex concentrate. Attempts to determine the origin of the bacterial contamination of field latex suggested that approximately 20% came from the tapping cut, 20% from the spout and 60% from the collecting cup. Further examination however led to the interesting observation that latex obtained from the tree by aseptic methods was already contaminated with bacteria.

Attempts to obtain sterile latex from the tree had already been made by McMullen[28] but depended on making small incisions in the bark so that only small amounts were obtained. In order to obtain larger quantities, Taysum built a metal box[29] around the tree, carefully sealing it to the trunk. Access to the tree was possible through a pair of rubber gloves with telescopic gauntlets, so that tapping could be carried out. The inside of the box and the surface of the tree was rendered sterile by irradiation with ultraviolet light (Figure 13).

Quite unexpectedly, it was found very difficult to obtain sterile latex by this means. If, however, the top half inch of the opened latex vessel was cut away at the time of tapping, sterile or near sterile latex was obtainable. Further investigation revealed the fact that in most trees under normal conditions of tapping, the top one third or one half inch of the opened latex vessels are contaminated with bacteria. In a few cases contamination was more widespread

and the trees were found to yield latex containing up to 4×10^5 viable bacteria per ml when opened aseptically eighteen inches below the tapping cut. Presumably bacteria had entered at the cut, and travelled down the laticiferous system. This high degree of contamination however, is not common.

The effect of bacterial contamination on the tree is by no means fully understood, but certain observations have been made which may prove of considerable value to industry. Trees which are comparatively heavily contaminated with bacteria have been found to have low yields, and the latex obtained usually shows a high bacterial count. The time of flow is often rather short.

Attempts were made by Taysum[30] to reduce the contamination by treating the tree with bactericides. These were applied in three ways, as aqueous dressings to the tapping cut, as suspensions in greases which were painted on the

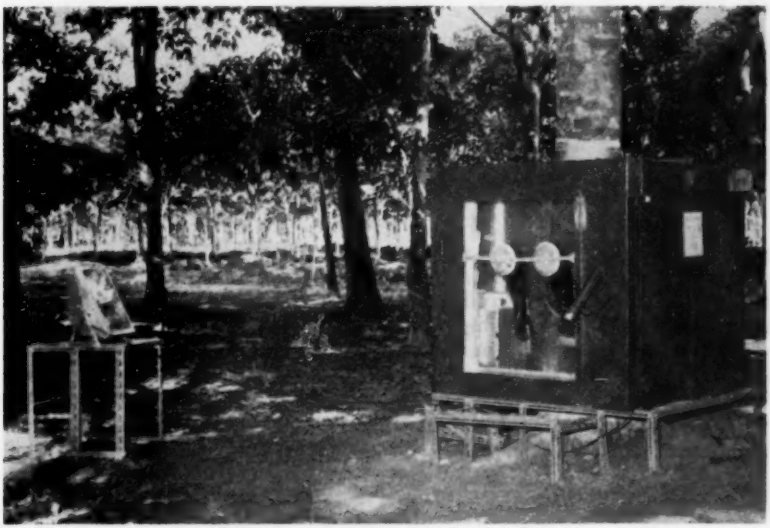


FIG. 13.—Tree with box for collection of latex under sterile conditions.[29]

tapping panel below the cut and as aqueous solutions or suspensions which were injected into the tree tissue at the tapping cut by means of a stout hypodermic needle. The results obtained were sometimes conflicting, but after a number of trials it is now concluded that each of these treatments gives increased yields of a latex which has a lower content of bacteria. The latex is sometimes much whiter in color and sometimes has a higher dry rubber content. Larger scale trials were then undertaken in which the tapping panel was treated with a mixture of chlorinated phenols and xylenols, and antibiotics carried in vaseline. Results of such a trial[30] are recorded in Table 1, and show the effect upon yield of rubber obtained.

The effect of bacteria upon the properties of latex concentrate are also by no means fully understood. It is of course well-known that unless adequate preservation is adopted and bacterial proliferation is hindered, poor quality results with high volatile fatty acid content (vfa number), high KOH number, and low

TABLE 1

FIELD TRIAL [30] COMPARING TREE TREATMENTS WITH GROWTH REGULATOR AND WITH BACTERICIDE/ANTIBIOTIC MIXTURES

Mean yield per month in lbs/task/tapping. Figures in brackets give yields expressed per cent mean yield for the task concerned throughout 1957

Treatment	Mean 1957	Mean for the seven months following treatment in May 1958	Mean for the seven months following treatment in November 1958	Mean for the six months July–Dec. 1959 (no treatment since Nov. 1958)
		First replication trees per treatment		
(1) Control	19	20.4 (107)	17.1 (90)	24.1 (113)
(2) Growth regulator 2,4,5- trichlorophenoxyacetic acid	22	27.1 (123)	23.2 (105)	28.3 (129)
(3) Bactericide/antiboitic mixture.	23	25.9 (113)	21.6 (94)	23.6 (103)
(4) (2) and (3) together	22	26.9 (122)	22.1 (100)	25.9 (118)
		Second replication trees per treatment		
(1) Control	18	18.2 (101)	15.7 (87)	19.2 (107)
(2) Growth regulator 2,4,5-trichlorophenoxyacetic acid	18	23.5 (131)	19.4 (108)	19.3 (107)
(3) Bactericide/antibiotic mixture	17	27.2 (160)	26.7 (157)	26.0 (153)
(4) (2) and (3) together	16	23.5 (147)	24.8 (155)	21.8 (136)

TABLE 2

IMPORTANCE OF BACTERIA IN PRODUCTION OF VOLATILE FATTY ACIDS [31]

Treatment of latex		Initial	2 days	4 days	7 days	14 days	21 days	28 days
Ammonia 0.2%	VBC[a]	—	2×10^5	2×10^5	3×10^5	2×10^5	6×10^4	5×10^5
	vfa[b]	0.01	0.01	0.10	0.19	0.22	0.22	0.25
Ammonia 0.7%	VBC	—	1×10^2	1×10^1	5×10^1	10	10	10
	vfa	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ammonia 0.2% and bactericide	VBC	—	<10	<10	<10	<10	<10	<10
	vfa	0.01	0.01	0.01	0.01	0.01	0.01	0.01

[a] VBC = viable bacterial count (number of bacteria per ml).
[b] vfa = volatile fatty acid number.

TABLE 3

INHIBITION OF VOLATILE FATTY ACID FORMATION IN LATEX BY BORIC ACID WHEN THE SAMPLES CONTAINED AMMONIA (0.20%), BORIC ACID 0.20% AND LAURIC ACID 0.03%

Sample reference number		Initial	After 1 week	After 1 month	After 3 months
F.29/105	Viable count	—	6.5×10^4	1×10^3	9×10
	vfa number	0.02	0.02	0.02	0.02
P 98	Viable count	3×10^4	2×10^3	1×10	1×10
	vfa number	0.01	0.01	0.02	0.01
P 148	Viable count	4×10^5	3×10^3	9×10^2	5×10
	vfa number	0.01	0.02	0.02	0.01
P 220	Viable count	3×10^5	7×10^4	2×10^4	—
	vfa number	0.02	0.03	0.02	—
H 5615	Viable count	3×10^4	9.5×10^4	2×10^3	—
	vfa number	0.02	0.02	0.02	—

mechanical stability (ASTM). It has been demonstrated that viable bacteria are largely responsible for vfa formation; thus in latex rendered sterile or nearly sterile[31] by the addition of sufficient ammonia or other bactericide little or no vfa develops on standing (Table 2). The development of high vfa content is always associated with a comparatively high bacterial count[32]. On the other hand the presence of a large number of bacteria does not necessarily entail the development of vfa. This is particularly the case in boric acid latexes, where the boric acid[33] appears to inhibit vfa formation (Table 3). Bacteria which appear to play a major part in vfa production are[34]:

Aerobacter aerogenes
Bacillus cereus var. *mycoides* (slow)
Bacillus subtilis (slight)
Bacterium mycoides (slight)
Butyribacterium sp.
Clostridium perfringens (slight)
Escherichia coli
Intermediate type 1 *coliform*
Micrococcus aurantiacus (slow)
Micrococcus luteus (slow)
Micrococcus sp.
Propionibacterium zeae
Proteus vulgaris
Pseudomonas sp. (slight)
Serratia indica (slight)
Serratia marcescens
Streptococcus faecalis
Streptococcus lactis

As well as producing volatile acids, bacteria are known to give rise to 'fixed' organic acids and may play a part in the development of the acids estimated by the KOH number titration other than volatile ones; even so the major part of these acids probably arise from chemical and enzymic processes.

A further possible effect of bacteria is attack upon protein and phospholipid materials which stabilize latex particles. A few cases have been examined where low mechanical stability was found to be associated with high incidence of *Bacillus subtilis*, a proteolytic bacterium, which it is thought may be responsible for the low stability[34].

In normal field practice latex received in the factory often contains more than 1×10^7 bacteria per ml. On standing through the day this figure rises steadily and thickening of the latex usually starts at a population of about 1×10^9, which is soon followed by coagulation. Sterile latex will remain

TABLE 4

YEARLY AVERAGE VFA NUMBERS OF SAMPLES OF COMMERCIAL CONCENTRATED LATEXES TESTED AT R.R.I.M.[a]

Estate	1954	1955	1956	1957	1958	1959
A	—	0.06 (16)	0.02 (34)	0.05 (22)	0.04 (3)	0.04 (59)
B	0.04 (22)	0.05 (61)	0.01 (90)	0.01 (107)	0.01 (84)	0.01 (11)
C	0.10 (104)	0.05 (35)	0.09 (12)	0.02 (7)	0.04 (11)	0.02 (14)
D	—	0.03 (5)	0.01 (32)	0.01 (33)	0.02 (31)	0.01 (26)
E	0.05 (10)	0.02 (14)	0.01 (19)	0.02 (19)	0.01 (12)	0.02 (14)
F	—	0.02 (35)	0.02 (43)	0.02 (49)	0.01 (50)	0.03 (36)
G	0.11 (11)	0.04 (14)	0.02 (32)	0.02 (36)	—	0.02 (9)
H	—	0.01 (32)	0.01 (27)	0.02 (7)	0.01 (18)	0.02 (9)
I	0.09 (25)	0.03 (42)	0.01 (44)	0.02 (31)	0.01 (1)	0.02 (9)
J	0.02 (12)	0.03 (3)	0.05 (13)	—	0.01 (12)	0.01 (19)
K	0.05 (23)	0.10 (9)	0.02 (2)	0.02 (9)	0.02 (5)	0.01 (12)

[a] Figures in parentheses indicate the number of samples tested.

fluid for several days. Since latex contains nutrients ideal for the proliferation of bacteria the producers of latex concentrate are up against a difficult problem in keeping their latex, utensils, plant and factory clean and free from bacteria. Great advances have been made in field and factory hygiene during the past decade as can be seen from the comparatively low values for vfa found in shipments made during recent years (Table 4).

LATEX PRESERVATION

For many years latex concentrate has been prepared by centrifuging or creaming field latex in the presence of ammonia, which preserves the latex, killing many of the bacteria present. After centrifuging, the ammonia content is about 0.2 per cent of the total concentrate and is then increased to 0.7 per cent for preservation during shipment and storage. The use of ammonia has many advantages, quite apart from its value as a bactericide. Destabilizing magnesium ions are precipitated as magnesium ammonium phosphate; fatty acids liberated by hydrolysis are converted into surface active ammonium soaps which increase the colloidal stability of the system; acids liberated by bacterial, enzymic or chemical activity are neutralized to ammonium salts, so that the destabilizing effect of their hydrogen ions is reduced. As a preservative am-

monia is volatile and so easily removable, leaving no solid material behind when latex is dried to rubber.

Ammonia also has disadvantages. It is comparatively expensive to use and is very unpleasant to handle even in dilute solutions. In using latex concentrates industrially it is often found that the 0.7 per cent ammonia present is first reduced to about 0.2 per cent or less; this small amount is retained not because it is difficult to remove, but owing to the fact that the presence of ammonia plays an essential part in the manufacturing processes for which latex is employed.

While carrying out systematic observations on the bacterial populations formed in field and concentrated latexes, the question of adding bactericides for their elimination was considered, and it became obvious that systems more powerful than ammonia could be adopted, probably with advantage. This led first to an examination of neutral preservative systems which however were not very promising and were soon followed by systems containing low levels of ammonia, about 0.2 per cent based on the latex, in combination with one or more additional bactericides. This level of ammonia was adopted because it represents the amount remaining in latex concentrate when it leaves the centrifuge, and is also a convenient level for a number of manufacturing processes.

A wide range of substances has been examined for use as secondary bactericides and many of them have been eliminated for one reason or another; a surprisingly large number of reagents still remain however, as possible and even promising preservatives.

For purposes of examination, latex concentrate is usually contaminated with an innoculum taken from another latex known to contain a broad spectrum of bacterial species. After addition of the preservative, latexes are stored in closed containers and tested at intervals over a period of six months or longer.

Antibiotics[35] and sulfonamide derivatives[36] are among the substances recently investigated. At the levels up to 10 parts per million, neither class of material was found successful. At higher levels, more than 100 parts per million, mixtures of antibiotics such as streptomycin, terramycin, aureomycin and penicillin were found to reduce the putrefaction occurring in latex concentrate as judged by the content of volatile fatty acids produced, provided they were activated with metal ions, such as silver, copper or zinc. Mixtures of sulfa drugs, such as sulfonamide, sulfathiozolmin, sulfaguanidine, sulfathiazole, sulfamerazine were found useful at levels over 500 parts per million but again only when activated by metal ions. Needless to say, the use of these substances at such a high level of concentration was far too costly and could in no way be justified by the advantages gained. It is of interest to note that preparations with sulfonamides often showed higher mechanical stability than comparable ones with antibiotics; the latter were found to depress stability in a number of trials, but did not invariably do so.

Derivatives of flavine such as acriflavine and proflavine were found to be effective at comparatively low levels, 0.01 per cent. Unfortunately the intense yellow color which they impart to the latex renders them unsuitable for commercial use.

A number of chlorinated phenols and bis phenols have been found effective preservatives. The use of sodium pentachlorphenate has been known for many years, but is not always regarded favorably owing to its high toxicity which renders effluent disposal difficult both from producing and from consuming factories. Among the other chlorinated and bis phenols found to be valuable bactericides in latex are the following:

2-Chloro-5-methylphenol
2-Allyl-3,5-dimethyl-4-chlorophenol
p-Chloro-m-xylenol
4-Chloro-2,3,5-trimethylphenol
4,6-Dichloro-2,5-dimethylphenol
2-Hydroxy-3,5-dichloro-4,6-dimethyldiphenylmethane
8-Hydroxy-3,5-dichloro-4,6-dimethyldiphenylmethane
5,7-Dichloro-4-Indanol
2,4,6-Trichlorophenol
Trichloro-*m*-cresol
2,4,6-Trichloro-3,5-dimethylphenol
2,4,6-Trichloro-3-methyl-5-ethylphenol
Tetrachloro-*m*-cresol
2,2′-Dihydroxy-3,5, 5,′5′-tetrachlorodiphenylmethane
Mixed chlorinated xylenols
Actamer (2,2′-thiobis-4,6-dichlorophenol)
Dichlorophen (2,2′-dihydroxy-5,5′-dichlorodiphenylmethane)[81]
Hexachlorophene (2,2′-dihydroxy-3,5,6,3′,5′,6′-hexachlorodiphenylmethane)

These substances are effective at levels between 0.05 and 0.2%.

Needless to say, although latex concentrates prepared using the above reagents with about 0.2 per cent ammonia and sometimes with a small amount of a detergent such as ammonium laurate have given concentrates showing excellent laboratory behavior, very few have yet been established as suitable for commercial preparation and shipment.

Another group of chemicals which have been found effective preservatives are accelerators of rubber-sulfur vulcanization. This is an interesting observation and may prove convenient in that the latex preservative can later be turned to good account in assisting vulcanization of the rubber. The following substances have been found useful, at levels ranging from 0.05 to 0.2 per cent:

Mercaptobenzthiazole (zinc salt)
Benzthiazolyl disulfide[37]
Tetramethylthiuram disulfide
N,N′-Dimethyl-S-carbethoxydithiocarbamate
Selenium diethyldithiocarbamate[38]
Zinc dialkyldithiocarbamates[39, 40].

Peroxides have also been found useful as preservatives. Substances such as hydrogen peroxide are dangerous commodities to handle and ship to producing countries like Malaya. Organic peroxides are still difficult but some appear more suitable for transport. Cumene peroxide is one of the most suitable found so far. Difficulties with peroxides arise when latex is used soon after preparation, since the raw rubber has poor aging properties. Three months after preparation, however, the latexes yield rubber which behaves normally.

Quaternary ammonium compounds are well-known as powerful bactericides. Unfortunately being cations these compounds are readily absorbed at the negatively charged surface of the rubber particles thus conferring a positive charge. This lowers the zeta potential at the rubber water interface and reduces stability. Only limited amounts of quaternary compounds can thus be added to ammoniated latex and insufficient is usually present to be an effective bactericide. Excess of quaternary compounds of course, converts natural latex into

a positive charged colloid which is stable to acids[41], and has limited commercial application.

One of the most interesting groups of materials examined for preserving latex comprises metal salts and complexes. A number of metals such as silver, copper, zinc[42], cadmium, nickel, bismuth; thallium, mercury, are effective in reducing bacterial activity in latex. Thallium and mercury are highly toxic and thus too dangerous to use; even compounds which are harmless when added to latex may liberate harmful substances under conditions of processing and of service. Copper is dangerous because of its catalytic activity in oxidizing rubber hydrocarbon. Of the metals used so far zinc is one of the most effective and appears one of the most likely to be employed commercially. It is not yet understood how zinc behaves, but it may be due to the formation of complex ions with ammonia. Compounds which have been found effective include zinc salts, such as nitrate or chloride, zinc oxide, and organic zinc compounds as mentioned above when referring to accelerators of vulcanization. The amount required ranges from about 0.05 per cent to 0.2 per cent.

In connection with these observations on metals, it has been noted that metal sequestering agents sometimes improve the stability of systems containing ammonia and bactericide. Examples are ethylenediaminetetracetic acid (EDTA)[43], polyphosphates, and oxine (8-hydroxyquinoline) which is particularly effective in the presence of zinc oxide[44]. Here again complexes with metals will be formed in the latex and may be the active agents. A number of derivatives of oxine have also been found promising such as merquinox (phenylmercury-8-hydroxyquinoline) and iodochloro-8-hydroxyquinoline[45]. These materials are effective at very low concentrations ranging from 0.005 to 0.05 per cent.

The majority of the above reagents have been examined only from the point of view of reducing bacterial and other undesirable changes occurring in latex concentrate after preparation. They have been selected by technological laboratory tests as promising substances from hundreds of systems examined. Their suitability for use as preservatives in commercial production of latex concentrate has in most cases not yet been investigated. A good preservative system has to fulfill many requirements beyond inhibiting the growth of microorganisms. It must not greatly affect mechanical stability, foaming behavior, coagulation and wet gel strength, and must not affect the properties of the rubber produced from the latex such as vulcanization characteristics or behavior on aging. It must be colorless, nontoxic, and nonstaining in rubber goods made with the latex. The testing of new preservative systems for latex concentrate is thus a laborious and time consuming operation and much work has to be done before the final selection can be made with any certainty.

Low ammonia latex systems which are now being produced commercially include the following recipes: zinc diethyldithiocarbamate[40], sodium pentachlorphenate[94], EDTA and sodium pentachlorphenate[43] and boric acid[46] alone or with a small amount of further bactericide such as sodium pentachlorphenate.

The latter system is rather an interesting one in that boric acid inhibits the formation of volatile fatty acids (vfa) even although viable bacteria are present as already discussed (see Table 3). Production control thus cannot depend solely upon vfa measurement but should either include a check on viable bacteria present or should make use of a further bactericide to ensure that proliferation does not occur during shipment.

Preservative systems for latex concentrate are becoming more complex. The most satisfactory ones will probably be those that ensure a quick and com-

plete kill of all bacteria present. To do this effectively one powerful all-round bactericide may perhaps be found, but it appears more likely that a system comprising two, three or more substances may offer the best and cheapest solution.

DRYING OF RUBBER COAGULUM

The major part of latex harvested from the hevea tree is of course converted to dry rubber. For this purpose field latex is treated with acid soon after receipt at the factory, allowed to set to a coagulum which is then machined through a roller mill, drained, and dried in specially constructed houses.

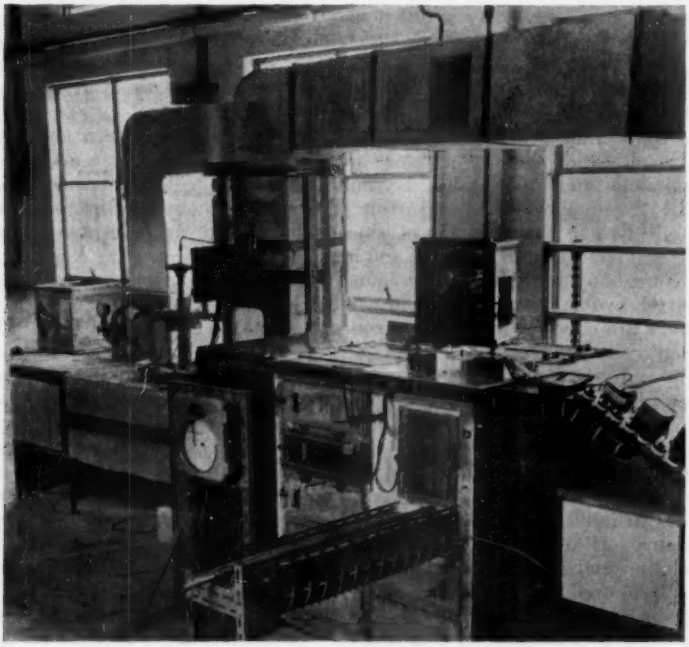


FIG. 14.—Experimental drying tunnel according to Gale.

The drying of rubber represents only a small fraction of the cost of production, (circa 2%), and until recently has received comparatively little attention as a research project apart from the work of Piddlesden[47] in 1937 who established two separate stages of drying, a rapid reduction in water content to about 10 per cent followed by a period when drying was very slow; he suggested that drying occurred largely by a diffusion mechanism.

During recent years the problem of drying has received further attention, chiefly because many estates are completing their program for replanting with high yielding strains of hevea and firewood is becoming increasingly scarce. This arises naturally as the ratio of rubber yield per acre to the number of old trees felled becomes greater. In consequence, oil-fired drying has been introduced. The cost of fuel for drying rubber has thus increased and considerable

efforts have been made to reduce cost by improvement in design of drying houses. In attempting to design a more efficient drier the need for further basic data on the effects of temperature and humidity on drying rates and on quality of rubber became apparent and during the last year or two a comprehensive study of drying has been made by Gale[48, 49, 50] using a specially constructed drying tunnel (Figure 14).

The type of drying curve found for natural rubber[99] is shown in Figure 15. This records the change in water content with time of coagulum, when subjected to an air stream maintained at known temperature and humidity. The drying curve may be divided into three stages. In the first, the sheet rapidly attains the wet bulb temperature of the drying air and remains steady for some time, while water is lost by evaporation and dripping; transport of water to the surface is brought about by syneresis of the rubber hydrogel. The temperature

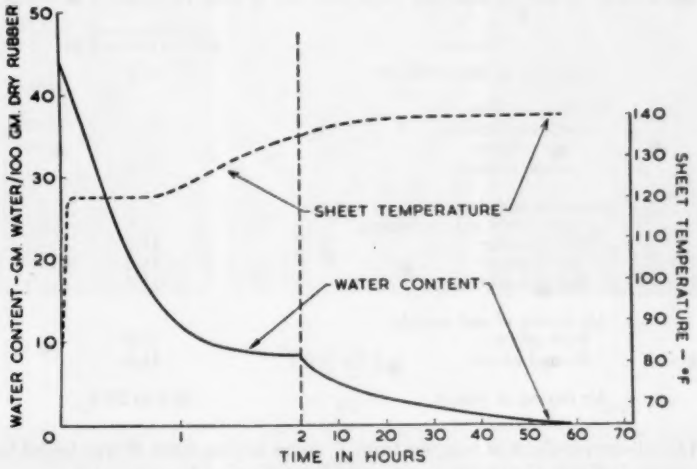


FIG. 15.—Typical curve[99] showing change in water content and temperature of wet rubber sheet with time, at 140° F.

of the sheet, which was recorded by a thermocouple placed in the latex before coagulation and machining, and thus firmly embedded in the sheet, then increased rapidly to within a few degrees of the dry bulb temperature of the drying air. During this second transitional stage of rapidly rising temperature, it is concluded that surface water must be disappearing from the sheet, as the supply of water from the interior of the sheet becomes less.

The third stage then commences in which water removal is controlled by diffusion from the inner parts to the surface of the sheet, and the rate of drying is very low. In this stage a gradual rise in temperature is observed, which slowly approaches the dry bulb value for the drying air. This stage normally occupies 85 to 95 per cent of the total drying time, during which the water content is reduced from approximately 15 per cent to 0.5 per cent.

Thickness t of the sheet dried had a marked effect upon drying time, θ, during the third and main drying stage, such that

$$\theta = B \cdot t^n,$$

where B is a constant for any one combination of temperature and humidity, and n was found to have an average value just under 2.1 This is a little greater than the value of 2.0 which would be expected if simple diffusion, uncomplicated by other factors, was the mechanism controlling the rate of water removal[51].

The situation is complicated, however, as shown by the interesting observation that within the range of sheet thickness studied (1.6 mm to 3.2 mm) the equilibrium moisture content of rubber in contact with air of a given humidity increased with thickness. This observation may be connected with the greater loss of serum substances per gram of rubber from a thinner sheet which occurs by syneresis of the wet coagulum and by washing during machining to a sheet.

TABLE 5

ACTIVATION ENERGIES FOR THE DIFFUSION OF WATER IN VARIOUS SYSTEMS

System	Activation energy B T U $\times 10^{-3}$/lb mole
Air drying of sheet rubber	17.2
Sorption of water by	
—smoked rubber	12.6
—para rubber	17.6
—crepe rubber	17.3
Sorption and desorption of water by starch gel containing:	
0.8% water	17.6
6.3% water	14.6
14.1% water	11.3
Air drying of cod muscle	
First phase	13.0
Second phase	15.8
Air drying of wheat	23.2 to 29.4

The observed effect of temperature, T, upon drying time, θ, was found to be represented effectively by an equation of the following type:—

$$\theta = C\, e^{(E/RT)}$$

where C is a constant for any one combination of humidity and sheet thickness. This equation accords with the requirements for an activated diffusion mechanism, which is likely to hold during the third stage of drying. The activation energy for the water content range 15 per cent to 0.7 per cent was calculated as 17.2×10^3 B.T.U./lb.mole and is compared with values obtained for other systems[50] in Table 5.

Increase in the relative humidity of the drying air prolonged the drying time required for removal of water during the diffusion drying stage. Thus the drying time at 40 per cent RH (rubber hydrocarbon) was roughly half the time required at 70 per cent RH. This is an interesting observation since it disproves a long held view that decreasing the humidity of the drying air caused the formation of a dry, moisture impermeable skin and thus decreased the rate of drying. The fact that humidity of the drying air markedly influences the rate of drying suggests that the aqueous vapor pressure may be the driving force within the sheet which causes diffusion of water through the rubber. In

this connection it is of interest to note that the energy of activation derived from these studies is numerically close to the value of the latent heat of water.

It has not been possible to analyze numerically the relation between aqueous vapor pressure within the sheet and the rate of drying, because of many complicating factors. For example it has been observed that during the later

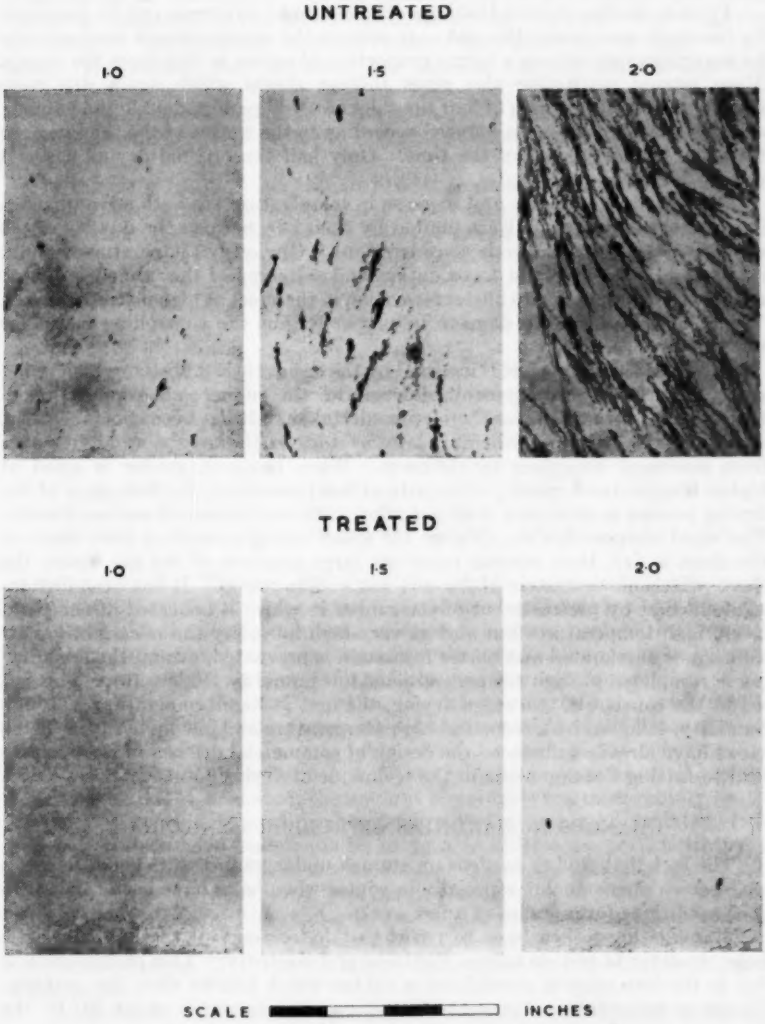


FIG. 16.—Rubber sheets showing prevention of bubble formation by initial treatment at high humidity during drying at 140° F.

stages of drying salts diffuse from the surface towards the middle of the sheet, thus modifying the vapor pressure gradient.

Four facts emerge from this work which are of importance for the economic drying of rubber. Syneresis of coagulum can contribute materially to the reduction of water content. Increase in humidity can seriously reduce the rate of drying. Increase in temperature can reduce drying time. Decrease in thickness decreases the drying time.

Further studies showed that loss of moisture by syneresis can be increased by thorough machining; this not only reduces the serum content mechanically by mangling, but induces a larger proportion of serum to drip from the sheets. More intense machining also gives thinner sheets which again dry more quickly. Although sheets of half the thickness will require double the hanging space, the time of drying is reduced according to the square of the thickness, so they dry in one quarter of the time. Only half the original drying space is thus required.

Reduction in humidity and increase in temperature are both advantageous in speeding up drying, but are limited by their effects upon the quality of the rubber as well as by economic considerations. Obviously temperatures cannot be so high as to give rise to oxidation and softening of the rubber; a further complication occurs due to blister formation in the sheet at higher temperatures. Technological and visual damage to rubber is thus the controlling factor for temperature increase.

A serious loss in revenue is incurred by the occurrence of blisters which under present marketing arrangements downgrades the rubber; an examination of their mode of formation was therefore undertaken. It has been concluded that carbon dioxide naturally present in latex as it leaves the tree[52] normally escapes from machined coagulum by diffusion. When however, rubber is dried at higher temperatures, more particularly at low humidities, the first stage of the drying process is short and does not allow sufficient release of carbon dixoide. The rapid temperature rise (Figure 15) which occurs as soon as the outside of the sheet is dry, then releases relatively large amounts of the gas within the sheet, which blows blisters in the soft wet middle region. It has been demonstrated[49] that by pretreatment of the rubber in which it is heated at comparatively high temperatures but also at very high humidity the release of gas by diffusion is accelerated and blister formation is prevented, even if the final drying is completed at high temperature and low humidity (Figure 16). This has led to the concept of two stage drying, the first at high temperature and high humidity, followed by a second at high temperature and low humidity. These views have already influenced the design of commercial driers and are likely to lead to further developments in the technique of drying rubber.

CHANGES IN HARDNESS OF RUBBER ON STORAGE

The fact that rubber hardens on storage under temperature conditions is a well-known phenomenon, especially in winter when bales have been exposed to cold conditions for a period of a few weeks.

Manufacturers then have to resort to "de-freezing" of the hard, inelastic bales, in order to restore normal hardness and elasticity. This phenomenon is due to the formation of crystallites in rubber which follows when the material is kept at temperatures below the transition temperature at about 30° C; the crystallites can be melted by an appropriate increase in temperature.

It is not so well known that rubber hardens on storage in quite another way,

the phenomenon being irreversible. This type of hardening occurs under tropical as well as temperate conditions and attains a steady value during the first few months after preparation. When Technically Classified rubber was first introduced by French producers in Indo-China in 1949 and later by producers in Malaya, the properties selected for classification purposes were Mooney viscosity and vulcanization behavior. After trial for a year or two, classification on the basis of Mooney viscosity had to be dropped, because the values as measured in the producing territory did not agree with the value measured by the consumer when he received the rubber two or three months later. The rubber had hardened, the amount varying considerably from sample to sample.

This phenomenon has also been known for a long time and in 1927, de Vries[53] suggested it might be due to changes in the nonrubber substances known to be present.

In the early 1950's Wood[54] studied the changes which occur when rubber is stored, and confirmed the observations of Messenger[55] that moisture inhibited the hardening effect. The effects of storage were accelerated by keeping rubber at elevated temperatures and under vacuum or dehydrating conditions; such treatment commonly resulted in irreversible increases in Mooney viscosity

TABLE 6

	Mooney viscosity of dry rubber		Gel content, %		Williams plasticity before and after Aging D_{10} m.m.			
					Alone		With TEP added	
Aeration	Alone	With TEP added	Alone	With TEP added	Before	After	Before	After
Nil	78	80	2	4	4.8	3.6	4.8	3.7
14 hrs	82	85	15	23	4.3	1.8	4.1	2.0
48 hrs	80	84	18	31	3.9	Liquid	3.8	3.9
172 hrs	69	75	18	40	3.2	Liquid	3.3	3.9

of 30 to 40 units. The removal of acetone soluble materials and proteins did not prevent the changes taking place. It was concluded that the hardening was associated with the development of a crosslinked benzene insoluble gel structure throughout the rubber, and suggested that the crosslinking might be initiated by the presence of peroxide or similar free radical forming groups.

Recent work by Sekhar[56, 57, 58] has helped to elucidate this phenomenon and leads to some interesting speculations on the nature of the natural rubber molecule.

When harvested under normal conditions latex often contains small amounts of peroxides. If it is aerated, the amount of peroxide increases rapidly for the first two or three days and reaches an equilibrium value. Estimates of the peroxide present have been made by using it to initiate the polymerization of methyl methacrylate in the presence of amine reduction activators.

When rubbers are prepared from aerated latex, they may thus be expected to contain peroxides. The results of tests to examine such a series of rubbers[57] are recorded in Table 6, which also shows the effect on properties of added tetraethylenepentamine (TEP) to the latexes thirty minutes before drying down to solid rubber.

These results indicate that with increased aeration and thus increased peroxide, two opposing reactions are occurring. Crosslinking is proceeding, as shown by increase in the gel content, and chain scission, as shown by the de-

crease in Williams plasticity value. Mooney viscosity appears to reflect both processes, first showing a minor increase and later a more marked decrease in value. When TEP is added to the peroxidized latex, it can be expected to activate the peroxides and give rise to crosslinking as has been demonstrated by Bloomfield[59]. This is indeed the case, a much higher proportion of gel rubber being formed. At the same time, much less breakdown of the rubber is shown by the Williams plasticity and Mooney viscosity values.

It thus appears that peroxides in rubber can lead to crosslinking reactions or to chain scission, depending upon circumstances; in most cases both reactions probably proceed simultaneously. While crosslinking arising from peroxy free radicals may account for part of the changes in rubber during storage, it does not account for the changes observed by Wood when rubber is heated under conditions of low humidity. This was demonstrated clearly by

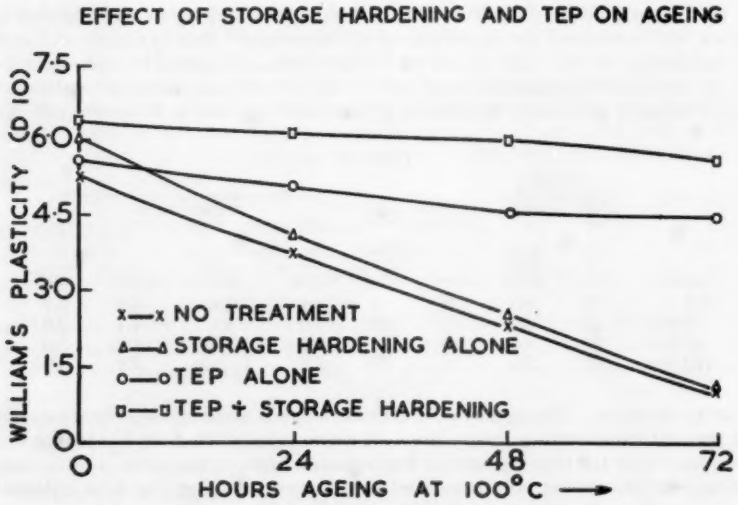


FIG. 17.—Effect of accelerated stroage hardening[57] and of TEP upon aging.

Sekhar in an experiment[57] in which aerated latex rubber was subjected to accelerated storage hardening (48 hours at 144 degrees F over phosphorus pentoxide in vacuo) with and without the addition of TEP, and then subjected to aging in air by heating as thin sheets at 100 degrees C. The data[57] are given in Figure 17, and show that although the rubber is harder after accelerated storage, it still degrades as rapidly or more so when aged. This indicates that the active groups responsible for degradation are not removed by the accelerated storage treatment and are different from those causing storage hardening. This view is supported by the observations on rubbers with TEP added, which show that the crosslinking brought about by TEP activation is additive to that brought about by accelerated storage. It was concluded therefore that two types of active groups occur in natural rubber, one peroxidic in character, the other unknown, but possibly capable of undergoing condensation reactions.

Further evidence was obtained from an experiment in which dry rubber was prepared from fresh latex to which increasing amounts of formaldehyde had

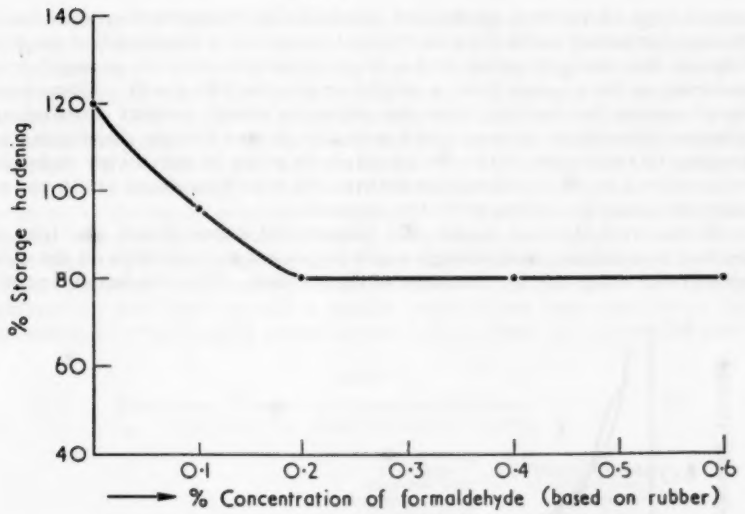


FIG. 18.—Decrease in hardening[57] of rubber by formaldehyde addition.

been added. It had already been shown[60] that formaldehyde deactivates the reduction activator in natural latex, and was thus anticipated that hardening[57] resulting from peroxy free radicals should decrease as the content of formaldehyde was increased. This was found to be so as demonstrated in Figure 18. After excess formaldehyde had been added, however, and hardening arising from peroxide had been prevented, accelerated storage resulted in a smaller but still substantial increase in Mooney value of 80 per cent, which presumably was due to the second type of activity postulated.

Experiments carried out to determine the nature of the second type of activity[57] lead to the interesting observation that mono functional primary amines inhibited storage hardening, whereas most bifunctional amines did not and even enhanced the effect; examples are given in Table 7. Since the substances found effective were all aldehyde reagents, the possibility that the

TABLE 7

Agent used for treatment, 0.5% on rubber	Mooney viscosity (small rotor)		Increase in Mooney viscosity, %	
	Before storage	After accelerated storage	By treatment	By accelerated storage after treatment
Nil (control)	38	83	—	118
o-Phenylenediamine	40	42	5	5
p-Phenylenediamine	72	88	90	22
Benzidine	70	85	84	21
Diaminohexane	50	84	31	68
Ethanolamine	40	44	5	10
Cyclohexylamine	40	45	5	12
Benzhydrylamine	40	43	5	8
Hydroxylamine	38	39	0	3
Semicarbazide	38	40	0	5
Dimedone	38	40	0	5

second type of reactive groups are aldehydic in character was considered. Storage hardening could then be brought about by a condensation reaction between the aldehyde group and a labile hydrogen atom on a neighboring molecule, as for example from a methyl or α-methylene group. Mono functional amines by reacting with the aldehyde would prevent crosslinking, whereas bifunctional amines would probably induce further crosslinking by reacting in two stages, first with an aldehyde group in one rubber molecule, followed by a second condensation between the remaining amino group and an aldehyde group in a different rubber molecule.

If this were the case, excess of a bifunctional amine should also tend to prevent crosslinking, since enough would be present to react with all the aldehyde groups using only the first stage of the reaction. This was demonstrated[58]

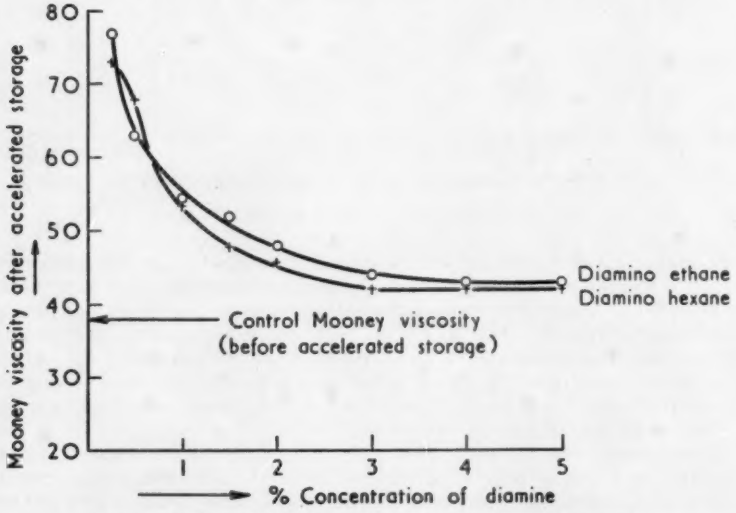


FIG. 19.—Effect of bifunctional amines on hardening[58] produced during accelerated storage of rubber.

to be the cases as shown in Figure 19, which shows the changes in Mooney viscosity after accelerated storage in the presence of increasing amounts of two bifunctional amines, diaminoethane and diaminohexane.

The reaction between rubber and two well known aldehydic reagents was then examined, hydroxylamine and 5,5-dimethylcyclohexane-1,3-dione (dimedone) which were added to latex in increasing amounts, and the amount of each required to inhibit storage hardening estimated. Since one hydroxylamine molecule and two dimedone molecules react with one carbonyl group, critical concentrations of these two reagents should be in the ratio of 69.5 to 280 or 1:4.0. For three different rubbers examined the values were 1:4.3, 1:4.0, and 1:4.4 respectively.

An attempt was made to estimate the number of aldehyde-reacting groups in natural rubber obtained from different types of trees (or clones). Rubber molecular weight was determined from viscosity measurements and the amount of aldehyde reacting groups calculated from the quantity of hydroxyl-

amine required to inhibit their activity. The number of active groups per molecule[58] ranged from 9 to 29, as shown in Table 8 and is sufficient to account for the variation in extent of hardening found for different rubbers on storage. The frequency of occurrence of the aldehyde reacting group thus ranges from one for every 1500 to one for every 500 isoprene units respectively, and suggests that there may be irregularities in the polyisoprene chain at rather long intervals. It is of interest to note that synthetic *cis*-polyisoprene (Shell) does not show the crosslinking reaction with bifunctional amines, and of course shows no hardening on accelerated storage[62]. The reactive groups may perhaps be formed in natural rubber during biosynthesis for example by a switch in the type of addition of the precursor molecule. An alternative explanation is that they arise from enzymic oxidation of methyl groups after the rubber hydrocarbon has been formed; a similar reaction has been established for cholesterol, in which methyl groups appear to be oxidized enzymically to alde-

TABLE 8

ESTIMATED NUMBER OF ALDEHYDE-REACTING GROUPS IN RUBBERS FROM DIFFERENT CLONES

Clone	Molecular weight in millions calculated from intrinsic viscosity ($\eta = 5.06 \times M^{0.67}$)	Estimated number of aldehyde-reacting groups per molecule of rubber
Avros 157	0.708	10
PB 23	1.023	18
A 44	1.000	15
Tjir 1	1.047	12
Avros 152	0.891	16
RRI 501	0.776	18
Glen. 1	0.851	20
War 4	0.891	9
SR 9	0.891	13
Rub 93	0.955	17
PB 186	0.977	14
SAB 24	1.047	15
Avros 256	1.072	12
Mixed latex from smallholding	1.148	29

hyde and carboxyl and are finally removed completely, being replaced by hydrogen[61]. The aldehyde reacting groups may also have some connection with the presence of high proportions of microgel rubber found in latex from newly tapped or rested trees[62] in both of which rubber has been stored for considerable periods and opportunity for crosslinking has occurred.

Preliminary shipments of small amounts of rubbers treated with amines to avoid changes in plasticity have been successful but more work is required before establishing that the process is suitable for commercial application. The economics of the process have also yet to be considered.

S.P. RUBBERS

The advantage of adding certain materials to rubber stocks to assist factory processing is well known and processing aids specially designed for this purpose have been available commercially for years. It is more than ten years now since work in Malaya first demonstrated the processing advantages gained by the incorporation of vulcanized latex particles into raw rubber[63]. These studies lead to the marketing of a series of rubbers termed Superior Processing, or S.P.

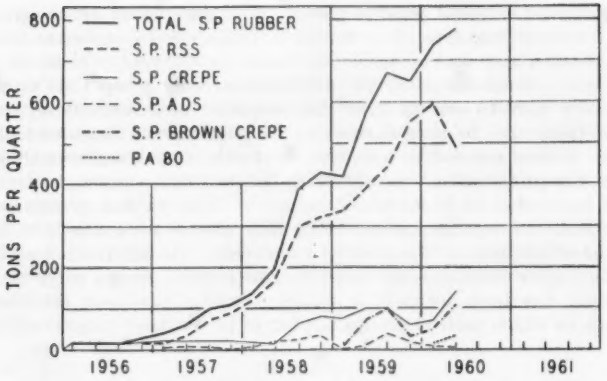


FIG. 20.—Quarterly shipments[98] of SP rubber 1956 to 1960.

Production[98] of these materials has increased steadily over the past few years as shown in Figure 20; current rate of production of all types is 3,500 tons a year.

More recently a concentrate or masterbatch has been produced which by admixture with any grade of raw rubber, natural or synthetic, will confer improved processing characteristics. This concentrate, known as PA. 80, is now available commercially and is finding an increasing application in manufacturing processes[64].

Table 9 shows the marked improvement[64] in die swell which is obtained by using PA. 80 to replace part of the natural rubber in whiting compounds made with a number of off-grade rubbers.

Figure 21 compares[64] the extrusion of white stocks made with cold SBR to which SBR 1009 and PA. 80 had been added. The improved surface finish and retention of die shape is clearly seen. Improved physical properties were also obtained.

A comparison[65] between PA. 80, SBR 1009 and other processing aids showed that in the compound used, maximum processing benefit was conferred by 60 phr of PA. 80 and by 40 phr of dark factice. PA. 80, however, gave considerably better physical characteristics in the vulcanizates, although the cost was

TABLE 9

PA 80 IN OFF-GRADE RUBBERS

Compound: Rubber 100; zinc oxide 5; stearic acid 1; MBTS 1; DPG 0.1; Nonox EXN 1; whiting 75; sulfur 2.5; mixed to 7¼ min. cycle in intermix; vulcanizing ingredients reduced by 20 and 40% when PA 80 is used to replace normal rubber by 25 and 50%.

	Mooney viscosity			Die swell (%)		
PA 80, phr	Nil	25	50	Mil	25	50
RSS 1 (YO)	43	44	61	46	18	8
RSS 3	46	49	64	46	18	8
RSS 5	39	47	56	34	17	6
Nigerian B2 sheet	33	42	54	42	17	6
Smoked blanket crepe	34	43	59	45	9	5
2X brown crepe	45	50	59	47	21	6
No. 4 remilled crepe	30	39	52	25	13	5
Flat bark crepe	21	33	43	28	20	6

greater. In mixtures prepared with PA. 80 and with brown factice designed to give equivalent tension characteristics, the costs were found to be similar, but PA. 80 gave better compression set.

One of the advantages of using vulcanized latex to give S.P. characteristics is thought to arise from the excellent dispersion which is obtained by mixing at the latex stage and coprecipitating vulcanized and raw rubber particles. Attempts were made to incorporate a variety of materials into rubber by mixing them as a suspension with raw rubber latex followed by coprecipitation with acid and drying as crepe or crumb. A number of materials such as wood flour, poly(vinyl alcohol), casein, and gelatin were found to give excellent S.P. characteristics and are being studied further with the hope that less costly rubbers having S.P. properties can be produced in this way[66].

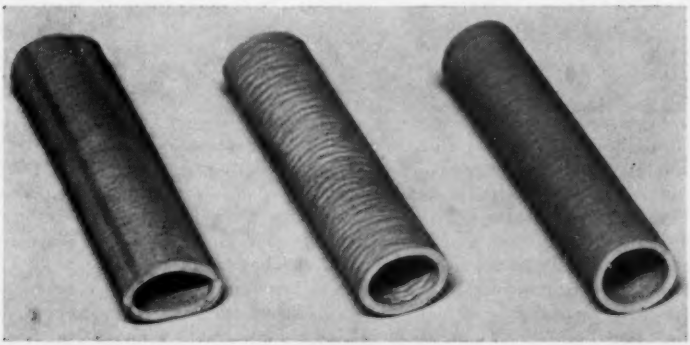


FIG. 21.—Extrusions[41] of white stocks made with cold SBR (left) to which SBR 1009 (middle) and PA 80 (right) has been added. Improved surface finish and retention of die-shape are noteworthy.

GRAFT POLYMERS

Graft polymers prepared by polymerization of suitable monomers in natural rubber latex have been known for a number of years[67, 68]. Those with styrene and with methyl methacrylate have attracted most attention and a very small commercial interest in the latter materials has developed, both as dry rubber and in the form of graft rubber latex.

Methyl methacrylate natural rubber grafts (or MG rubbers) range from tough elastomers to plastics with high impact strength, and show excellent physical properties, but are expensive and cannot compete in price with the much cheaper high styrene-butadiene resins and other plastics save for rather specialized applications.

More recent studies have indicated that as originally prepared by allowing monomer containing the peroxide initiator to react with latex containing a reduction activator (polyamine), the rubber particles appear to form grafts which aggregate in the surface layers, possibly due to the fact that the rubber hydrocarbon molecules in these layers are more accessible to attack from the aqueous phase. Alternative methods of preparation in which rubber soluble initiators were used, as opposed to water soluble ones[69], permitted a more uniform production of graft throughout the particle. Similar results were obtained by aeration of latex, which produced peroxides group on the hydrocarbon of the rubber particles *in situ*, and thus would be expected to give more uniform graft-

TABLE 10

SINGLE AND MULTI-STAGE GRAFT POLYMERIZATION
INTRINSIC VISCOSITY OF SIDE CHAINS PRODUCED
BY ORGANIC PEROXIDE ACTIVATION

Two stage process		One stage process	
MG 10 + 10	0.23	MG 20	0.51
MG 15 + 15	0.33	MG 30	0.76
MG 20 + 20	0.64	MG 40	0.85
MG 25 + 25	0.99	MG 50	1.42

INTRINSIC VISCOSITY OF SIDE CHAINS PRODUCED
BY AERATION ACTIVATION

Multi-stage process		One stage process	
MG 20	0.4		
↓			
MG 30	0.59		
↓			
MG 40	0.54		
↓			
MG 50	0.57	MG 50	2.2

ing throughout the rubber globule[70]. The characteristics of the original and modified methods of preparation are clearly seen in improved film forming characteristics and in greater wet gel strength when foam rubbers are prepared from graft rubber latexes. Further advantages have appeared in the shape of lower viscosity solutions and better adhesive characteristics which are being utilized industrially to a small extent in adhesives manufacture.

The most recent studies by Sekhar have been concerned with the molecular weight of the secondary polymer side chains attached to the main rubber hydrocarbon "backbone"[71]. Changes in initiator concentration had little effect on side chain molecular weight in grafts containing 25 per cent or less added monomer. Changes in monomer concentration produced differences, however, and it was therefore argued that multi-stage grafting to produce MG rubbers should give side chains having molecular weights different from those given by a single stage process. This view was confirmed by two experiments, one using added peroxide, the other aeration to initiate polymerization, as shown in Table 10.

It will be seen that much shorter side chains and therefore a larger number

TABLE 11

PHYSICAL PROPERTIES OF METHYL METHACRYLATE GRAFT RUBBER
VULCANIZATES PREPARED BY SINGLE AND BY MULTISTAGE
POLYMERIZATION

Composition	Process	Tensil, kg/cm²	Modulus, 100%, kg/cm²	Modulus, 300%, kg/cm²	Hardness, °B.S.	Elongation, %	Tear B.S., kg
MG 30	One stage	250	45	140	85	489	18
Rubber 70	Five stages	220	69	158	97	400	19
Methyl methacrylate 30	Ten stages	220	72	164	98	385	25.5
MG 40	One stage	239	59	165	95	420	25
Rubber 60	Five stages	204	94	190	99	350	26
Methyl methacrylate 40	Ten stages	207	99	190	99	351	29
MG 50	One stage	170	96	—	98	250	29
Rubber 50	Five stages	221	123	—	99	286	36
Methyl methacrylate 50	Ten stages	207	132	—	99	225	39

per unit length of rubber "backbone" can be produced by multistage grafting. In the case of MG 50 rubbers (containing 50 parts methyl methacrylate, 50 parts rubber), side chains averaging one quarter the length were formed by a four stage process. This difference in molecular weight can be expected to modify the physical properties of vulcanizates prepared with the grafts and are shown in Table 11.

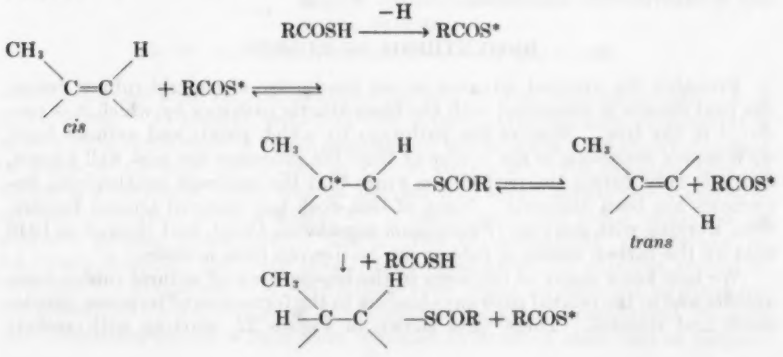
The stocks prepared by multistage grafting were found to be very hard and in the case of MG 50, the multistage stocks had to be milled for more than the normal period in order to prevent mold distortion during vulcanization. The data show that when a greater number of shorter side chains are present, vulcanizates have considerably higher modulus, greater hardness and higher tear strength. Tensile strength is reduced in the case of MG 30 and MG 40, but is not reduced in the case of MG 50. It is of interest to note that the 40 per cent compound prepared by multi-stage grafting has modulus, hardness and tear strength similar to those of the one stage 50 per cent compound, but shows considerably greater elongation and higher tensile strength.

It is apparent that multistage grafting, which results in shorter side chains, has yielded a series of copolymers having somewhat different properties from the earlier ones produced by the one stage process. As well as having academic interest, these observations may have industrial applications; the latter, however, still remain to be investigated.

cis-trans ISOMERISM

One of the characteristics of natural rubber is to crystallize when stored at low temperatures. The rate of crystallization at temperatures from 0° to −50° C is greatly retarded by vulcanization, but even so, crystallization occurs rapidly enough to make rubber lose its flexibility and become unserviceable within a few hours or days. Crystallization is thought to be a nucleation process; vulcanization represses crystal nucleation in the region around a cross-link, as well as reducing mobility of the chain segments, and so hinders both crystal formation and growth.

In the course of studies to hinder crystallization by adding side groups to the main hydrocarbon chain, it was observed by Cuneen and his coworkers that certain thiolacids gave far greater retardation than could be accounted for by direct addition[72, 73]. This observation led to the view that reduced crystallization was brought about by *cis-trans* isomerization, the mechanism being as follows:



The addition reaction goes to completion when the double bond is opened on one side by a thiolacid free radical and on the other by hydrogen from a second thiolacid molecule which then becomes a free radical itself. In this series of reactions a thiolacid free radical opens a double bond and becomes attached to the rubber hydrocarbon. At this stage, free rotation can occur, but the thiolacid can be split off, and the double bond may reform either in the *cis* or the *trans* position. Sulfur dioxide, butadiene sulfone and other reagents[74] show similar behavior with rubber hydrocarbon and markedly retard crystallization. Butadiene sulfone is particularly suitable for practical application since it can be milled into rubber and liberates sulfur dioxide when the temperature is raised, which then gives rise to *cis-trans* isomerization.

If the change from *cis* to *trans* can be accomplished, it was argued that the change from *trans* to *cis* should also be possible, and experiments in England with gutta percha demonstrated that the change could be brought about by reacting this *trans* form of the hydrocarbon with thiol acids or with sulfur dioxide. Starting with hevea rubber and gutta percha, products were obtained which showed similar physical characteristics and identical infrared spectra. It was estimated that under the conditions employed, the equilibrium between the *cis* and *trans* forms occurred at 43 and 57 per cent respectively[75, 76].

Further work in America has shown that treatment of natural polyisoprene with selenium had a similar effect in bringing about *cis-trans* isomerization[77]. Hevea rubber (*cis* form) and balata (*trans* form) were isomerized to a common structure intermediate between those of the two starting forms, as revealed by the infrared spectra. This *cis-trans* equilibrium was variously estimated as occurring at 50:50 or 60:40, thus showing a higher proportion of the *cis* form than that found by the English observers.

The effect of a small amount of *trans* units upon rate of crystallization is marked. Thus, vulcanized rubber containing 6 per cent of *trans* double bonds crystallized 500 to 1000 times slower at $-26°$ C than normal natural rubber[96]. In the case of rubber containing about 15 per cent *trans* it was not possible to detect crystallization in the stretched vulcanizate at $-26°$ C. It is fortunate that only a small proportion of *trans* double bonds are required to bring about major changes in crystallization since at about 15 per cent and above, there is a marked loss of tensile strength, probably due to lack of crystallization on stretching.

Practical application of this work is found in the anticrystallizing rubbers which resist hardening at low temperatures; these are now available commercially in experimental quantities.

BIOSYNTHESIS OF RUBBER

Probably the greatest advance in our knowledge of natural rubber during the past decade is concerned with the biosynthetic pathway by which it is produced in the tree. Most of the pathways by which plants and animals build up complex chemicals in the course of their life processes are now well known, but it is only during the past eleven years that the pathway synthesizing isoprenoids has been disclosed. Much of this work has centered around Bonner, who, working with guayule (*Parthenium argentatum Gray*), first showed in 1949 that all the carbon atoms of rubber can be derived from acetate.

We now know many of the steps in the biosynthesis of natural rubber from acetate and in the related pathways leading to the formation of terpenes, carotenoids and steroids. These[78] are shown in Figure 22, starting with acetate

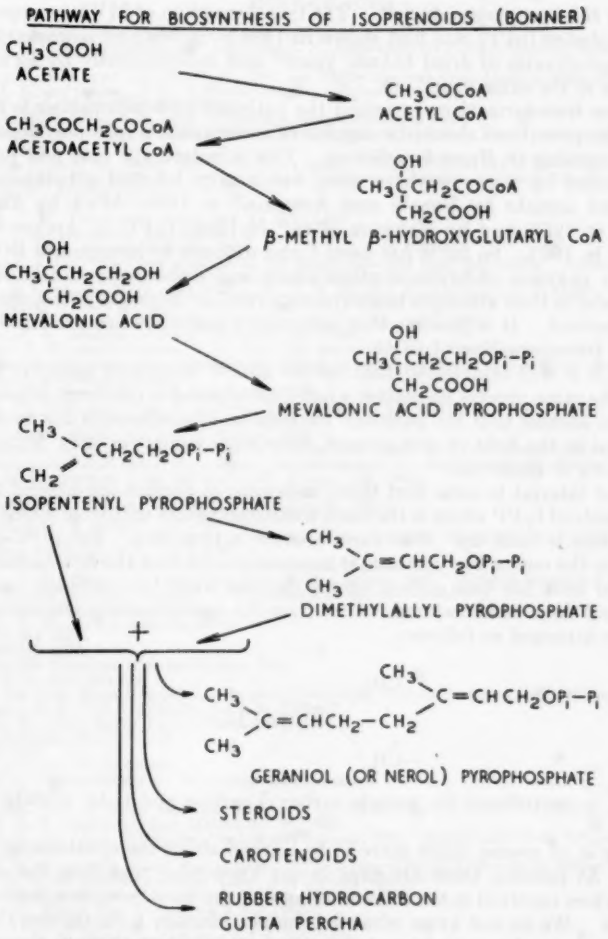


FIG. 22.—Pathway for biosynthesis of isoprenoids (after Bonner[79]).

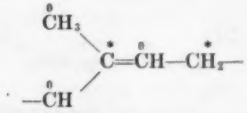
which is formed from carbohydrates by an already well established pathway of living things. At present, not every one of these steps has been demonstrated as occurring specifically in *Hevea brasiliensis*, but all have been shown to occur in plants or through the agency of animal enzymes[92]. For example, acetate occurs in a variety of plants and its activation to acetyl co-enzyme A and subsequent conversion to acetoacetyl Co A has been shown to be catalyzed by enzymes purified from spinach leaf[84]. The transformation of acetate to β-hydroxy β-methyl glutarate (BOG) is brought about by enzymes extracted from flax[85]. Mevalonic acid (MVA) has been found an essential nutrient for the growth of certain strains of *lacto-bacilli* and can be incorporated directly into cholesterol (which is built from the same five carbon atom unit as polyiso-

prene) by rat liver preparations[86]. The transformation of MVA to isopentenyl pyrophosphate (IpPP) was first shown in 1958 by Bloch and coworkers, using enzyme autolyzates of dried bakers' yeast[87] and independently by Lynen and coworkers in the same year[88].

If these transformations represent the pathway by which rubber is formed, each of the precursors should be capable of incorporation into polyisoprene by enzymes existing in *Hevea brasiliensis*. This is indeed the case and has been demonstrated by many workers using isotopically labelled substances; thus ^{14}C-labelled acetate by Bonner and Arreguin[83] in 1949; MVA by Park and Bonner[89] in 1958, and by Kekwick et al.[90] in 1959; IpPP by Archer and coworkers[91] in 1960. So far it has been found difficult to incorporate BOG into rubber by enzymes of hevea or other plants and Rabinowitz and Gurin were unsuccessful in their attempts to incorporate BOG or its co-enzyme A derivative into cholesterol. It is possible that alternative pathways are available at this point for transformation of BOG.

Since it is well established that nature almost invariably achieves a given step by the same process no matter what kind of plant is involved, it seems reasonable to assume that the pathway for iosprenoid synthesis is the same in all plants and in the light of our present knowledge comprises very broadly the steps shown in Figure 22.

It is of interest to note that three molecules of acetate are needed to form one molecule of IpPP which is the basic five carbon atom unit from which rubber hydrocarbon is built up. One carbon atom is thus lost. Using ^{14}C-labelled acetates in the one or two position, it has been shown that the five carbon atom isoprenoid unit has two carbon atoms derived from the carboxyl carbon of acetate and three carbon atoms derived from the methyl carbon atom of acetate. These are arranged as follows:



Where $\overset{*}{C}$ is contributed by acetate carboxyl carbon and $\overset{\circ}{C}$ by acetate methyl carbon[79, 80].

There is, of course, much more to be learned about the synthesis of natural rubber. At present, there are gaps in our knowledge regarding the enzymes and cofactors involved in the different stages of the transformation from acetate to rubber. We do not know what determines whether a *cis* (rubber) or *trans* (gutta percha) polymer is formed; how the process of synthesis is stopped and why some rubber chains are longer, some shorter; why fresh rubber shows reactive groups and trees on standing show a higher proportion of gel rubber than when in regular tapping. It seems very likely, however, that biochemical studies will solve many of these problems before long, although it is still a moot point whether a better understanding of the processes involved will enable us to modify and control the characteristics of the natural rubber molecule synthesized by the tree. Perhaps a more likely result is that we may be able to induce the tree to yield even more rubber than the present maximum.

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THE BREEDING OF HEVEA BRASILIENSIS *

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Over the past thirty-five years, a revolution has taken place in the plantation rubber industry. It was slow to start, but gradually gained momentum; during the last fifteen years its effects have changed the whole aspect of the industry. No small part of this change has been due to the efforts of a relatively few men working in tropical countries, often alone and independently of one another. These men are the breeders of *Hevea brasiliensis*.

Over those thirty-five years, probably no tree crop of any kind has undergone such spectacular improvement in yield as has the rubber tree of commerce. In 1925, a good yield from an acre of rubber trees was held to be about 500 pounds of dry rubber per year. Today, modern planting material is expected to reach a yield of 2000 pounds at maturity, four times as much. And there are distinct possibilities that this figure may be pushed still higher.

Now this is a remarkable achievement. It has had far-reaching effects not only on the economics of the industry itself, but also on the well-being of millions of people directly concerned with the production of natural rubber in many tropical countries. It is the purpose of this paper to give a brief account of how it has been done, and to outline some of the means by which it is hoped to make still further improvement.

EARLY HISTORY

Most people connected with the rubber industry are familiar with the rather romantic story surrounding the first introduction of Hevea to the Far East from its native home in Brazil; of how Wickham gathered the seeds on the banks of the Tapajos River near its confluence with the Amazon, and sent them to Kew Gardens in England in 1875; of how seedlings were despatched to Malaya and to Ceylon in the following year; and of their successful establishment there, followed by virtual neglect until about the turn of the century. Of the odd 2000 plants which were sent from Kew, it is probable that less than 50 ever survived and set seeds. These few trees have given rise to the millions of acres of plantation rubber trees in the world today. It is a matter of some wonderment and conjecture that the genetic potentiality for such improvement was resident in those few trees.

Compared with many other plants, breeding and selection in Hevea got off to a slow start. The principles involved are similar to those which had been used for many years, but it was not until about 1918 that the first scientific approach was made to the problem. Up to that time the planters had been busy with other problems—how to grow the trees, how to tap them, how to prepare the rubber for market. Moreover, market prices were high, and there was no great economic urge to improve yields.

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It is typical of plants (and animals) developed from seeds, that is by sexual means, that no two of the progeny are exactly alike; variation is characteristic. The early rubber planters soon observed that there was a tremendous variation in the yields of individual seedling trees in their plantations. It was found, for instance, that 30% of the trees were yielding 70% of the crop, and not all of this variation could be ascribed to environment. Seeds were taken from high yielding trees, but the resulting seedlings did not show much improvement in yield. It was in 1918 and shortly afterwards, that early breeders in Java and in Malaya made the first attempts to multiply high yielding trees vegetatively.

When we multiply a plant such as a rose or a geranium by rooting it from a cutting, we reproduce it vegetatively. No flowers or fruits are involved, and it can be reproduced indefinitely in this way. The characteristic feature of a group of individuals obtained from a single individual in this manner is that they are all exactly alike. They constitute what is known botanically as a "clone". Certain plants are not easily rooted from cuttings, but here the same result can be achieved by grafting or budding. In this case a piece of the desired plant is grafted or budded on to the rootstock of another individual, generally of the same species. The act of grafting merely perpetuates and multiplies the desired type; it does not change the intrinsic genetic constitution of that type.

Hevea is one of those plants which does not root easily from cuttings. However, it can be budded easily, and it was a natural step for those early breeders to select certain of their high yielding trees and to multiply each of them by budding, thus establishing as many clones as there were seedlings selected. They then had to wait five or six years for their budded trees to grow to tappable size, followed by three or four years of tapping and yield recording in order to find out what they had achieved.

The results were not always successful; some of the clones did not reproduce the high yields of the seedling trees from which they came. In such cases it was probable that the so-called "mother tree" had derived its high yield from its environment rather than from its intrinsic genetic quality. But in other cases it became apparent that a real step forward had been made. Instead of 500 pounds per acre per year, the early clones were capable of producing 800–1000 pounds. As time went on, and the significance of this new development became appreciated by the planters, the work was intensified. Vast numbers of seedling trees were examined, and clones made from them were compared and selected. Yields were pushed up above the 1000 pound level, and many of the clones used in the plantation industry today are still those selected thirty years ago. They frequently bear names of the research organizations or plantations which developed them, such as AVROS 50, Tjirandji 1, Prang Besar 86, Bodjong Datar 5.

Experience also showed that yield, though predominantly important, was not the only desirable character to be sought in a clone; some exhibited a tendency to break off in the wind, while others showed a poor resistance to certain diseases. And when the latex concentrate industry was developed, latex of some clones was found to be unsuitable for this process. Here were more problems for the breeder, and he is still trying to surmount them.

FURTHER DEVELOPMENTS IN BREEDING

Clones selected as described above are sometimes referred to as "primary" clones. They came from seedling trees found growing in a plantation, and in

selecting them the breeder had merely taken advantage of what nature had already provided. Having obtained such clones of proven merit, it was a logical step to combine their useful qualities by crossing them sexually, harvesting the seeds so obtained, growing the seedlings, and selecting the population after further vegetative multiplication. Clones made in this way are called "secondary" clones, and many of them are coming into general use today. It is hoped that they will yield near the level of 2000 pounds of dry rubber per acre per year at maturity.

Sexual crossing of two types of Hevea is not an easy matter, and the time necessary to develop and select a clone in this way is about twenty years. Few breeders have lived long enough in the tropics to see the process through from beginning to end. The flowers of the tree are tiny, and generally borne high on the branches, so that they may be reached only by a scaffolding or a step-ladder. Moreover, hand pollinations are best carried out during the heat of the tropical day, generally in bright sunlight. Male and female flowers are borne separately on the same tree, and the act of pollination consists essentially in transferring the pollen from the selected male parent to the stigma of the flowers of the selected female parent, while certain precautions are taken to ensure that foreign pollen is excluded. The percentage of success is never high, and for every 100 pollinations made, one may expect to harvest three to five fruits, each containing three seeds. Many good clones do not bear fruits prolifically even when naturally pollinated, and on these a zero result is often encountered. In such cases, crossings can be achieved by using these clones as male parents.

The seeds obtained from such crossings then have to be grown as seedlings, vegetatively propagated as clones, and further examined and selected for their desired characters of yield, wind resistance, disease resistance, latex quality and the like. And as has been mentioned previously, this process may require twenty years.

Since hand pollination is never attended by a high percentage of success, the population of seedlings at disposal for further selection is regrettably small. Any breeder knows that the greater the number of individuals he has for selection, the higher will be his chance of finding the "Napoleon". There is a means of attaining this end by the use of so-called "isolated seed fields", in which Nature is allowed to perform her own pollinations. Clones of the desired parents (generally two) are planted together in small plots in the forest or among other crops isolated from all other Hevea trees. Hevea is naturally insect-pollinated (by species of midges which do not fly very far) and crossing will occur between the two clones or parents in the field. If due care has been taken in selection of the parents, many seeds can be harvested, thus providing the high population so desirable for adequate selection. However, since one must wait five or six years from planting of these isolated seed fields until the trees are old enough to bear flowers and seeds, a similar period is added to the lengthy time already necessary for adequate selection.

So far, only clones have been mentioned as the modern planting material. Concurrently with clones, however, another type of material has been used extensively. This is the so-called high-yielding seedling family. It has been found that when certain clones are crossed sexually, they produce seedlings whose average yield is almost as high as the clones which produced them. Variation in individual yield is of the same order as found in unselected seedling populations, but the general level of yield is considerably higher. By planting such seedlings at high density, and by thinning out the lower yielders on criteria of girth and yield, the average yield of the remainder may be raised still further.

Yields of 1500 pounds per acre and more have been recorded from such seedling families. The seeds necessary for such plantings are produced in large seed fields, where two (or sometimes more) parental clones are planted in juxtaposition, thus ensuring cross-pollination between them.

Although clones are still favored for planting by most estate companies (mainly on account of their somewhat higher yield performance) they possess certain inherent disadvantages. The budded plants which constitute them are costly to produce, and require more attention in the nursery and in the field. As a rule they attain tappable size a year later than seedlings. Moreover, since all trees in a given clone are exactly alike in genetic constitution, they all tend to react in a similar way to their environment. If the clone is susceptible to wind damage, large numbers of trees may be lost in heavy winds; if it is susceptible to a certain disease, then environmental factors which favor that disease may spell the ruin of the clone. This can be serious when much time and money have been expended in establishing the clone and in waiting until it attains maturity. To lessen the risk attendant upon such disasters, the wise planter does not put all his eggs in one basket—he plants a number of the recommended clones.

On the other hand, the trees of the high yielding seedling family are not all alike. They vary in yield, in wind and disease resistance, and in their individual reaction to a given set of ecological conditions—soil, climate etc. Hence the chance of their succumbing to some untoward event is less than with clones. For the planter whose knowledge of modern plantation practice is scanty, whose capital is limited, and who is anxious for a quick return on his outlay to keep him in business, the seedling family holds some advantages over clones. In many of the new countries now clamoring for technical assistance in which rubber can be grown, enthusiasm for rubber as a crop can be engendered more easily and quickly if seedling families can be made available to the farmer.

RECENT DEVELOPMENTS IN BREEDING

Great strides have been made over the past thirty years, but the possibilities for further improvement are far from exhausted, and new horizons are opening up.

It has been mentioned that almost all of the vast areas of rubber trees under cultivation today have been derived from a relatively small number of trees which survived Wickham's original introduction. The wonder is that with so few, so much has been accomplished. Wickham's collection was made at a place called Boim, on the banks of the Tapajos River, shortly before it enters the great Amazon. It appears that his collection was an enormously lucky one. His seeds were of *Hevea brasiliensis*, the species of Hevea which makes the best rubber; moreover, it is now known that the *brasiliensis* type contains variants in other parts of the Amazon basin which do not yield as well as those which Wickham collected. He might easily have made his collection at some other locality, and come home with inferior seeds. One can only speculate what would have happened to the industry under such a circumstance.

Hevea brasiliensis and its related species are known to occur over a vast area of the Amazon Valley, from the mouth of this great river over northern Brazil, into the Guianas, Venezuela, Colombia, Bolivia and Peru, even up to the headwaters of the tributaries of the Amazon in the lower slopes of the Andes. Taxonomists now recognize about eight or nine species, of which may be mentioned *Benthamiana, pauciflora, spruceana, guianensis,* and of course *brasiliensis.*

All show wide variations in habit, in leaves, in flowers and seeds, in bark characteristics, and in quality and quantity of the latex they produce. However, all species have the same number of chromosomes, all hybridize fairly freely, and indeed natural hybrids are commonly met with in the region, to such an extent that precise classification of the genus was rendered confusing for a long time, and even yet causes differences of opinion among taxonomists.

It is this vast congeries of species and variants which offers a fertile field for further improvement in Hevea. It is obvious that Wickham's collection merely scratched the surface, and that the great genetic potentiality of the area has not yet been fully exploited.

As one aspect of this may be mentioned the existence of a serious disease of Hevea called South American Leaf Blight, caused by the fungus *Dothidella ulei*. Fortunately for the plantation rubber industry of the Old World, this disease is still confined to Tropical America. It is known that all descendants of Wickham's seeds (and hence all clones developed from them) are susceptible to the disease, and under certain conditions eventually succumb to it. Should a few spores of the fungus become established on Hevea in Africa or the Far East, a dismal prospect would confront the industry. And with steadily increasing rapidity and means of air travel, such a contingency cannot be lightly disregarded. It is a sword of Damocles which hangs over the head of the industry, and a challenge to the plant breeder.

A significant step forward was made in this matter in 1937. This was at the Ford Company's two plantations of Fordlandia and Belterra in Brazil, started in 1928 and 1934 not far from the site of Wickham's original collection of seeds fifty-three years previously. Ford's plantings of Eastern-type clones had shown progressive mortality from the disease, and a selection and breeding program was initiated in 1937. The loss of the Far Eastern rubber plantations by Japanese invasion during the Second World War stimulated a renewed interest in production of natural rubber in Tropical America, and in 1941 the United States Government entered into agreements with a number of Latin American Governments providing for co-operative breeding of Hevea against the disease, as well as for encouragement of rubber planting in the respective countries. Experimental areas were established in the co-operating countries, staffed by technical men of the U. S. Department of Agriculture (Rands and Polhamus[7].) At two centers, one in Costa Rica and the other in Guatemala, larger "regional" stations were established for concerted attack on the many problems.

Explorations of the Amazon Valley were carried out, and new genetic material was discovered and incorporated into the breeding program. Resistance to the disease was found among variants of *H. brasiliensis*, and also in some of the other species of Hevea, notably *H. Benthamiana* and *H. pauciflora*. However, none of the resistant types exhibited a yield comparable to that of Far Eastern clones, and thus they could not be used directly as planting material. It was realized that a solution of this problem lay in the initiation of a long series of crosses between high-yielding but susceptible types and low-yielding resistant types, with the aim of combining resistance with high yield in selections made among the progeny.

However, the years necessary for realization of such a procedure were poor comfort to those planters who had young plantings of susceptible clones doomed to die; nor was it much to offer those who wished to try the "new" crop in Tropical America. A partial solution was found in the use of the so-called "three-component" tree. The normal budded tree consists of two parts: a seedling rootstock, and a stem with its crown of foliage derived from the selected

high yielding clone, which has been budded to the rootstock near ground level. In the three-component tree, a second graft is made at a height of 6 to 8 feet above ground level, using a clone known to be resistant to the disease; this clone provides the branch framework and foliage of the tree. Provided the graft is made well above normal tapping heights, the yield of the intermediate portion (the high yielding clone) is not greatly reduced by the lower yielding capacity of the resistant crown, and such trees give good yields.

But the establishment of such three-component trees in the field is often a difficult procedure; grafting of young trees at high levels is frequently attended by poor success, requiring repeated rounds of grafting, and the operation may delay tappability of the tree by as much as two years. More importantly, while it has been applied successfully by estates having expert staff and financial resources, it has never been enthusiastically adopted by the smallholder without these advantages.

The series of crosses begun at Belterra in 1937 and widened in scope by technicians of the U.S.D.A. and of the Latin American Governments eventually showed tangible results. It became apparent that some of the progeny from first crosses did indeed combine the desired characters. Yield had been increased, and resistance was retained in high degree. The next step in the process was to infuse more yield into the selections, and this required another series of crosses. This time, the so-called "backcross" method of the plant breeder was generally adopted, in which the selected first crosses were crossed again with Eastern clones. The progenies from such an operation are termed "first backcrosses" or "first outcrosses". The process can be repeated into second and subsequent backcross generations, and actually this has already been done on a more or less arbitrary basis, for time has not permitted thorough assessment of the true worthiness of the first backcrosses involved. The important point about this work is that resistance to *Dothidella* is apparently conditioned by relatively few genes, for despite repeated backcrossing with susceptible Eastern clones, segregates among the progenies still exhibit a high degree of resistance.

It is now about twenty years since this program was initiated, and the first backcross clones emerging from the process were opened for tapping at the beginning of 1960. Early tapping results indicate that some of them exhibit high yields, but an additional tapping period is necessary for confirmation.

With the development of synthetic rubber and the end of the emergency caused by the War, interest in the program by the United States Government gradually waned. By 1954 the international co-operative work so enthusiastically begun in 1941 was virtually suspended. The main regional station in Costa Rica was abandoned, and the only breeding work now being done with the expenditure of United States money is being carried out in Guatemala by one or two rubber technologists working on a part-time basis under the aegis of the International Cooperation Administration. It is a sad commentary on the machinery of Government that the enterprise should have come to such a premature end.

Actually, it is not ended. For during the course of the work, distribution of early selections was made to various Latin American countries, and also to the U.S.D.A. Plant Introduction Station at Miami, Fla. With some danger from occasional frosts, Hevea can be grown at Miami sufficiently well to enable propagation of living material. The existence of the Station at Miami has served a most useful and necessary purpose. Direct transference of Hevea material from Tropical America to countries free of South American Leaf Blight

would carry with it the danger of introduction of the disease. At Miami, material received from Tropical America is budded on to old seedling trees already established there; when this has grown to usable size, budwood is cut and sent to final destination. The climatic conditions at Miami, prohibit survival of the fungus, so that risks of its transference is eliminated. From Miami, further distribution of resistant material has been made to the Firestone Plantations in Liberia and to research organizations in Malaya and Ceylon. From these centers in the Old World, additional distributions have been made.

Breeding and selection is now being carried on in a few Latin American countries, notably Brazil and Guatemala; but so far as is known, no organized attempt is being made to renew exploration of the Amazon Valley with a view towards diversification of the basic material so necessary in a well planned scheme of breeding. In Guatemala, Firestone set up an auxiliary breeding station in 1949, where selection work is now being actively pursued in conjunction with the Company's main center in Liberia. Goodyear is also vitally interested in the work, and carries out trials of selections on its plantations in Costa Rica, Guatemala and Brazil. In the main, it rests now with private companies in the plantation industry and with research organizations in the Far East to take advantage of the genetic material now available. While crossings can be made and tested for yield in disease-free countries, selections cannot be made for resistance in the absence of the disease. Consequently, representative material for such screening must be transferred to Tropical America for test. At the present time, Firestone is using its station in Guatemala for this work, and hopes to extend it to its plantation in Brazil. The research organizations in the Far East do not yet have a center in Tropical America for such a purpose, but Baptiste[1] and Hoedt[2] have recently made pleas for the establishment of such a center on an international basis. The Rubber Research Institute of Malaya[3] has recently opened a unit of the Institute in Trinidad for work on *Dothidella ulei*.

Apart from the interest attaching to selection for resistance to Dothidella and other diseases, another promising field for selection has been opened up. When crossings were made between Far Eastern clones and material collected from widely dispersed regions of the Amazon Valley, it was noticed that many of the progenies exhibited a remarkable vigor. This has been ascribed to "hybrid vigor", a phenomenon well known to breeders of plants and animals. Such selections display, at least in their early growth stages, a rate of development half as much again as that of most Eastern clones. It has been mentioned that all such Eastern clones must have originated from a relatively few trees surviving from Wickham's original collection; despite the great advances which have been made in yield improvement, a considerable amount of inbreeding must have been inevitable. And in Hevea as well as in many other plants, this may result in decreased vigor. The possibility, then, of infusing a renewed vigor into our high yielding clones is alluring. It has implications leading towards greater wind resistance and early maturity, both features of interest to the planter.

Still another virtually untouched field for selection in Hevea is one with which the author has been rather intimately connected. In any monoclonal stand of rubber trees (that is, where all the trees from ground level to topmost branches are genetically identical) the individual trees show variation in growth and yield. Some of this variation can be ascribed to local soil differences, but undoubtedly much of it is due to differences in vigor and yield of the

stocks on which the buddings grow. These rootstocks are of seedling origin, and no two of them are exactly alike. Reduction in this variation and also improvement in yield has been obtained by the use of seedling stocks derived from selected seedling families. But such stocks still vary considerably, so that differences in vigor and yield of the scions can be observed. If this variability could be reduced by the use of clonal rootstocks, it is conceivable that the general yield level of the planting could be raised very appreciably.

One approach to this problem is to grow Hevea from cuttings, and to produce "self-rooted" clones. But until recently, Hevea has resisted most attempts to root it in this way. However, on Firestone Plantations in Liberia, Levandowsky[3] demonstrated in 1954 that it could be done by using leafy cuttings taken from vigorously growing budwood of established clones, and subjecting them to special treatment under a mist spray. Roots were formed after 40–50 days, and rooted cuttings could be hardened off in small containers under gradually reduced shade, and successfully established in the field. However, there was considerable variation in rooting propensity of the clones used. Some rooted up to 50%, while others hardly rooted at all. Working in Malaya, Tinley and Garner[5] and Tinley[6] have since confirmed the work of Levandowsky on a greater range of clones, employing certain refinements in technique.

The rooted cuttings made in Liberia grew quite well when established in the field. Observation of these plants over four years, however, has shown that they do not produce a root system capable of anchoring the tree firmly in the soil. A multiple taproot system is almost invariable, and such roots grow obliquely downwards. But none of the self-rooted clones has produced the ring of surface lateral roots typical of the normal seedling rootstock. The consequence has been that the young trees wobble around in the soil, and all have had to be supported by stakes. After crown formation, moderate winds blow the trees over. Obviously such trees could never be grown to maturity without elaborate artificial support.

In order to describe one method of getting around this difficulty, it is necessary to outline something of the phenomenon frequently referred to as "juvenility" in Hevea. A normal budded tree presents an almost cylindrical stem, and the location of the graft is usually shown by a characteristic swelling near ground level. On the other hand, a typical seedling tree presents a tapered or conical lower stem which is preserved throughout maturity and old age. This lower portion of the stem of a seedling tree possesses some rather unique characters. If buds are removed from it and budded to other seedlings, then all the resultant buddings will exhibit the tapered shape of a seedling tree, and after a few years the location of the graft is hardly visible. On the other hand, if buds are removed from the upper stem or branches, then all the resultant buddings will show the nearly cylindrical stem of the normal budded tree. Moreover, shoots which arise from the lower stem of a seedling emerge at a narrow angle and are reddish-brown in color, while those which arise from the upper stem or branches emerge at a wide angle and are green in color. Yet another character of the lower portion of a seedling stem is that cuttings made from it can be rooted much more easily than those taken from higher portions of the stem.

In work carried out in Liberia by McIndoe[4] it was shown that these unique characters of the seedling are confined to a region extending from ground level to a height of about three feet, and that branches or shoots which arise between these levels also exhibit them. Obviously then, there resides in this lower portion of the stem some influence, or possibly substance, which confers these characters; its nature is as yet quite undetermined. Since the characters are

resident in the lower stem of old as well as young seedlings, the use of the term "juvenility" to describe the phenomenon may not be appropriate.

During the course of the work, it was also found that these characters can be transferred by budding. The next step was to apply these findings towards the production of rooted cuttings with a root system similar to that of normal seedlings. A number of nursery seedlings (2½ years old) were cut off near ground level, causing them to produce shoots which exhibited the tapered character. Buds were removed from the lower tapered portions, and budded to other seedling rootstocks. After the inserted buds had produced shoots, these shoots were ringbarked about two inches above their origin and covered with soil. After 30–40 days, rootlets were produced just above the ringbarked area; the rooted shoots were then cut off and planted in a development bed under mist spray, where they survived and grew well. We thus had produced a number of "rootstock" clones from a corresponding number of original seedlings.

On excavating the rooted cuttings at a later date, distinct clonal variations in root system were discernible. All clones showed multiple taproots in greater or less degree, which tended to grow vertically downwards. But in some of them, there was a marked tendency to produce a ring of sub-surface lateral roots quite similar to that found in the normal seedling rootstock. It is reasonable to assume that these surface lateral roots will provide the firm anchorage necessary for the growing tree. The clonal rootstocks were budded with several well known high yielding clones and established in the field, where they are now under observation. At the present time we know little about the inherent yield or growth-promoting capacity of the rootstock clones which have been set up; these qualities are likely to be of paramount importance in influencing the yield and growth of the clones budded on them. Experimental work designed towards selection of additional rootstock clones, and towards a rapid and practical means of propagating them, is now in progress. An intriguing possibility for the future is the development of clonal rootstocks from seedlings produced by crossing *H. brasiliensis* with *H. Benthamiana* or *H. pauciflora*. Such seedlings are known to exhibit extraordinary vigor, and if they possess a reasonably good yield, so much the better. Much work remains to be done on the subject, but herein lies the germ of an entirely new development in rubber culture.

PROBLEMS FOR THE FUTURE

Progress in Hevea breeding, for its full return in productivity, will demand increasing attention to improvement in soil conditions by rational fertilizer amendments and good cultural conditions. Indeed, outstanding advances in these matters have been made in recent years. Up to the present time, however, the chemist and physiologist have played little direct part in accelerating the slow process of Hevea breeding, and since there are certain avenues in which modern laboratory procedures may help, it is appropriate to indicate some of them here.

It has been mentioned above that a desideratum in the selection procedure is to have at disposal a large number of individuals from which the "Napoleon" may be chosen. We are now getting these large numbers by means of pollinations performed by Nature in isolated seed fields. But we know little of their individual potentiality until they are grown, generally as clones, in the field. After a number of years some selection is possible, but in the meantime a great deal of time, planting space and money have been expended on material which will be discarded. If we could find some reliable and rapid means of "early

yield prediction", and thus reduce our populations by discard of the least promising while still in the nursery seedling stage, much effort could be eliminated. A number of tests have been devised in the past, but their applicability is laborious and slow, or their reliability is under question.

Again, selection of progenies for resistance to South American Leaf Blight requires that the screening be carried out in some country where the disease exists. This means that representative material of progenies produced in Africa or the Far East must be transported to Tropical America for satisfactory test, and this is a troublesome and time-consuming business. Little is known about the mechanism of resistance, except that its basis is probably physiological rather than anatomical. If the substance or substances which condition resistance could be determined, then we might have a tool for selection in the absence of the disease.

Yet another field for investigation concerns the nature of so-called "juvenility" in Hevea. We know that the lower stem of a seedling possesses a number of unique characters not found in the upper parts of the plant, and that these characters can be transferred by budding. If they are conditioned by the presence (or absence) of some substance, its determination would lead towards a better understanding of stock-scion relationships, and may have some important practical applications.

It has been pointed out that hand-pollination in Hevea is never attended by a high percentage of success. Many clones are self-sterile, while some never set fruits when attempt is made to cross-pollinate them with other clones. In others, a good fruit-set may be obtained shortly after pollination, but many fruits cease to develop and drop off before maturity. Attempts have been made to influence this situation by application of various hormonal sprays, but results so far have been largely negative; success in the operation remains much as it was thirty years ago, and seems to depend on the skill of the operator, especially in his selection of flowers and parental material for pollination. Here then, is another field in which the chemist and physiologist might aid the breeder of Hevea.

CONCLUSION

The intrinsic yield of *Hevea brasiliensis* has been more than tripled over the past thirty-five years largely by the efforts of plant breeders. While it is not to be expected that progress will be as rapid over the next thirty-five years, yet the end is not in sight, and indeed new horizons are opening up. Coupled with the improvements made in other aspects of rubber culture, the industry is now in an excellent position to maintain its competitive status in world markets, and thus to contribute to the prosperity and economic stability of the tropical countries whose fortunes are so closely bound to it.

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THE STRUCTURE OF VARIOUS NATURAL RUBBERS *

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Although Columbus, on his second journey to America, found the natives playing with balls which bounced and were elastic, it was almost 300 years later before use was made in Europe of the gum used in these balls. Priestley found that it could be used for erasing lead pencil marks. However, when further applications of this material were attempted, it became recognized that rubbers from different parts of the country differed. These differences arose partly from the botanical origin of the plants from which the gum, or rubber, was collected and partly from the methods of collecting and preparing it. With the passage of time, fine Para rubber came to be recognized and used as the best rubber and it held this position until it was supplanted by plantation rubber from *Hevea brasiliensis* trees.

These differences in rubbers from different sources made it necessary for the user to know more about the material. Even the distinguished physicist Faraday[1] became involved in the problem and in 1826 he published an analysis of the latex and also the dry rubber. His results were as follows:

	Latex	Dry rubber
Rubber	31.3%	72.65%
Vegetable Albumin	1.8%	4.35%
Bitter material, rich in nitrogen	7.33%	16.35%
Extractable	2.90%	6.65%
Water	56.57%	0 %
	100.0%	100.0%

Thus determinations of the moisture content, the acetone extract of soluble non-rubber constituents, the nitrogen content to indicate the amount of protein and the ash to indicate soil and other contaminants were used to differentiate between different rubbers. Faraday's analysis is rather typical of Para rubber prepared by evaporating latex on a pole slowly rotated over an open fire. Plantation rubbers, prepared by sheeting or creping, or washed rubbers generally have smaller amounts of non-rubber constituents. The differences in physical properties and the differences shown by the above type of analysis resulted in the grade classifications of commerce.

Analyses, such as the above, offered no information about the obvious differences between rubbers of the Para type and those like balata. Probably Himly[2], in 1835, was one of the first to investigate the constitution of rubbers. From the destructive distillation of 19 different samples of rubber from different

* Original contribution. This paper was presented before the Division of Rubber Chemistry, ACS, at the Louisville Meeting, April 19–21, 1961.

botanical sources, he found the same distillation products and in the same quantitative proportions. Ten of these rubbers are described as: *Siphonia Cahucu, Siphonia elastica, Castilleja elastica, Cecropia peltata, Hippomane biglandulosa, Lobelia Caoutchouc, Ficus religiosa, Ficus indica, Ficus lymphaeaefolia* and *Artocarpus integrifolia.* Hence it seemed that the basic constituents of all these rubbers were the same.

Still the differences between gutta, balata and chicle, which are types of rubbers of commerce were not explained, even though it was known that the rubber hydrocarbon was C_5H_8, until these materials were studied by x-rays. Then it was found that, since there is one double bond for each C_5H_8 unit, balata exists in the *trans*-1,4 configuration whereas Hevea is in the *cis*-1,4 configuration. Chicle was found to be a mixture of the two. Further improvements in the structure determinations, made possible by infrared spectroscopy, have shown that Hevea is not completely *cis*-$C(CH_3) = CH$-but contains 2.2% of $CH_2 = C(CH_3)$- structure while balata contains 1.3%. This latter structure, in synthetic polyisoprenes, arises from 3,4 addition[3].

TABLE I

PARTICLE SIZE DATA FOR LATEXES OF NATURAL POLYISOPRENES

Latex	Particle Range, Å	Mode, Å
Hevea brasiliensis	1,000–15,000	1,200
Alstonia scholaris	1,300–5,300	3,300
Castila elastica	540–17,400	Not defined
Cryptostegia grandiflora	800–9,600	2,000
Ficus elastica	430–25,600	1,730 and 10,400
Funtumia elastica	860–5,000	2,500
Landolphia species	650–20,000	1,620
Manihot glaziovii	600–1,800	1,200
Mascarenhasia elastica	200–10,000	1,400 and 200
Palaquium philippinensis	25,600	—

Since the rubber, as obtained from the plant, is in the form of a latex, early investigations of the latex were carried out with the light microscope. The Brownian motion of the particles, particle shape and size and particle size distribution were investigated with several latexes. With the development of the electron microscope it became possible to study the particles in the latex in greater detail and this was done for the readily available latexes.

Heretofore most of the newer analytical methods have been applied mainly to Hevea, balata and Chicle since these are important substances of commerce and are most readily available. LeBras[4] has discussed some properties of some of the less well-known rubbers. It was the purpose of this investigation to apply some of these methods to less well-known rubbers and latexes in order to determine their similarities to the better known rubbers.

EXPERIMENTAL

When possible the plants were tapped and the latex collected as is done with Hevea. The latexes were stabilized with ammonium hydroxide or sodium pentachlorophenate.

The particle size distributions of the latexes were determined from electron micrographs of the latexes. Standard procedures were used for brominating the particle and photographing them. The particle size data are given in Table I and electron micrographs are reproduced in Figures 1 and 2.

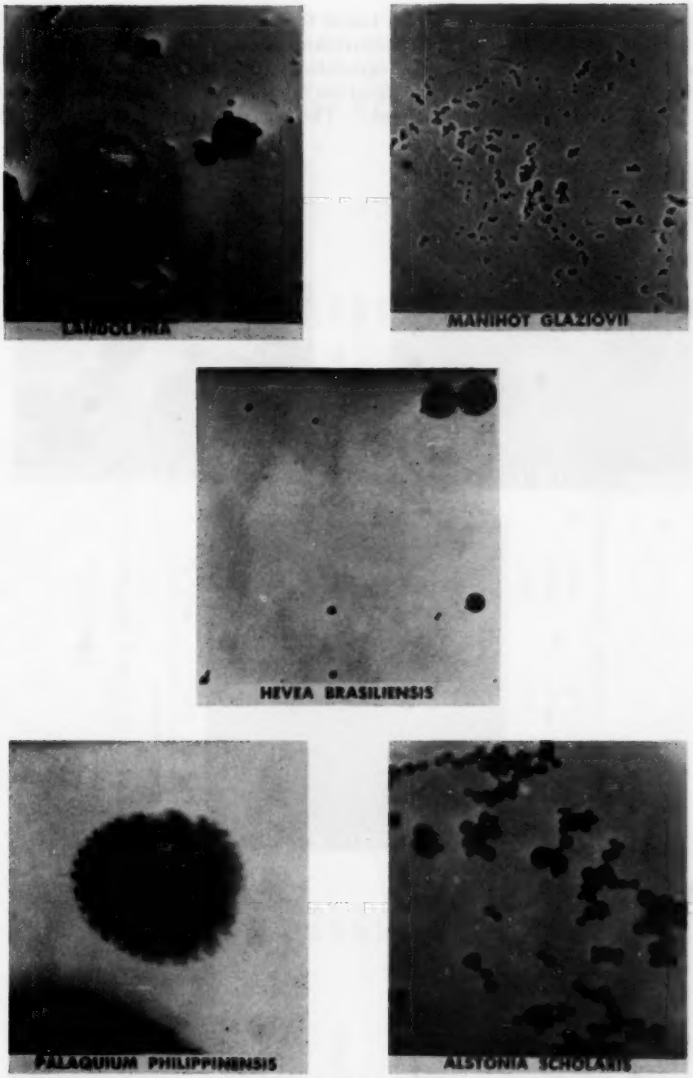

FIG. 1.—Electron micrographs of latexes.

Samples for determining the microstructures and x-ray diffraction photographs were obtained from the latexes, by coagulating in alcohol and then dissolving the coagulated material in toluene. Other samples of crude rubbers were dissolved in toluene and the insoluble material was separated by filtration. The clear toluene solutions of the polymers were digested with hot 5% HCl solu-

tion to remove protein. Care was taken to exclude air during the digestion. It was also necessary to have an antioxidant present during the digestion and prior to coagulation to prevent degradation. With some samples, hot 5% NaOH solution was used for the extraction because it was found that the emulsion which formed was easier to break. The digestion was carried on, periodi-

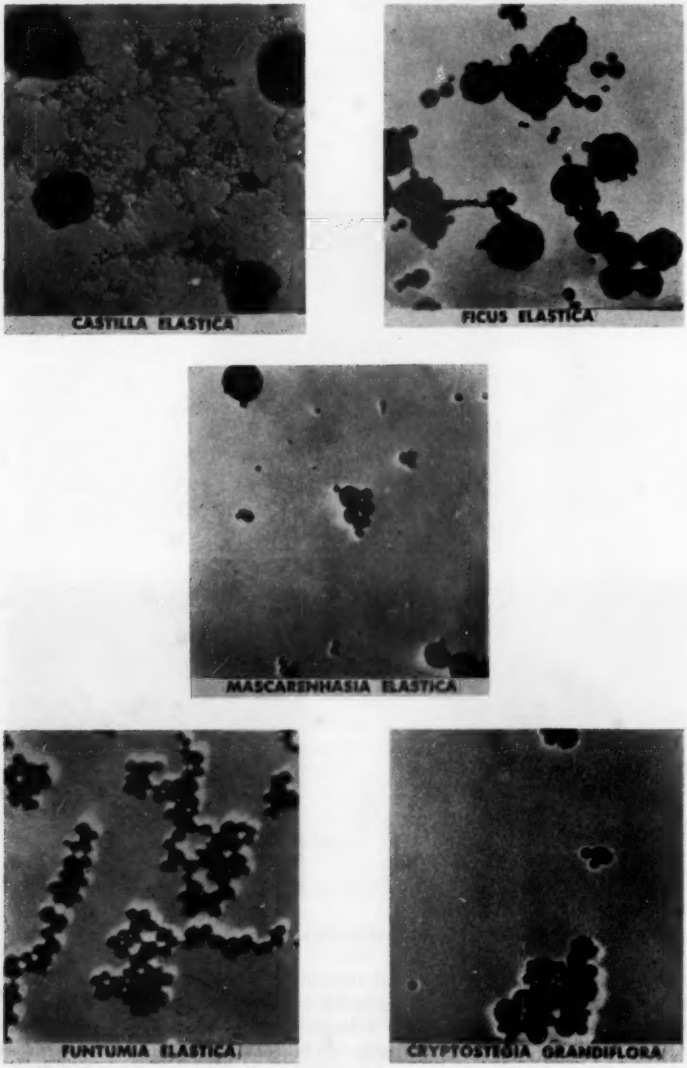

FIG. 2.—Electron micrographs of latexes.

TABLE II

MICROSTRUCTURE AND X-RAY DIFFRACTION OF NATURAL RUBBERS

Name	IR Microstructure *				X-Ray		Inherent Viscosity	Gel, %
	Cis 1,4%	*Trans* 1,4%	3,4%	T.F., %	Cryst.	Ext. %		
Hevea brasiliensis	97.8	0.0	2.2	95.0	V. strong	600	8	0
Alstonia scholaris	97.8	0.0	2.2	82.8	Could not stretch		—	—
Castilla elastica	97.6	0.0	2.4	96.2	None	600	1.9	33
Castilla ulei	97.0	0.8	2.2	102.2	V. weak	770	—	—
Clitandra orientalis	97.7	0.0	2.3	98.0	None	675	3.0	31.5
Cryptostegia grandiflora	97.7	0.0	2.3	96.7	Strong	370	—	—
Ficus elastica	97.6	0.0	2.4	97.4	Trace	600	3.1	14
Funtumia elastica	97.6	0.0	2.4	95.3	V. strong	900	1.7	24.3
Hancornia speciosa	97.6	0.0	2.4	97.0	Trace	775	0.3	11.5
Landolphia species	97.6	0.0	2.4	97.4	Strong	900	3.2	12.5
Manihot glaziovii	97.6	0.0	2.3	102.2	V. strong	600	—	—
Mascarenhasia elastica	97.7	0.0	2.3	98.3	V. strong	600	—	—
Parthenium argentatum (Guayule)	97.8	0.0	2.2	95.7	Strong	300	1.3	23.8
Achras zapote (Chicle)	22.2	76.5	1.3	102.3	V. strong	0	0.6	0
Balata and Gutta Palaquium philippinensis	0	98.7	1.3 all *trans* (from spectrum)	95.0	V. strong	0	—	—

* No. 1,2 addition was observed in any of the polymers.

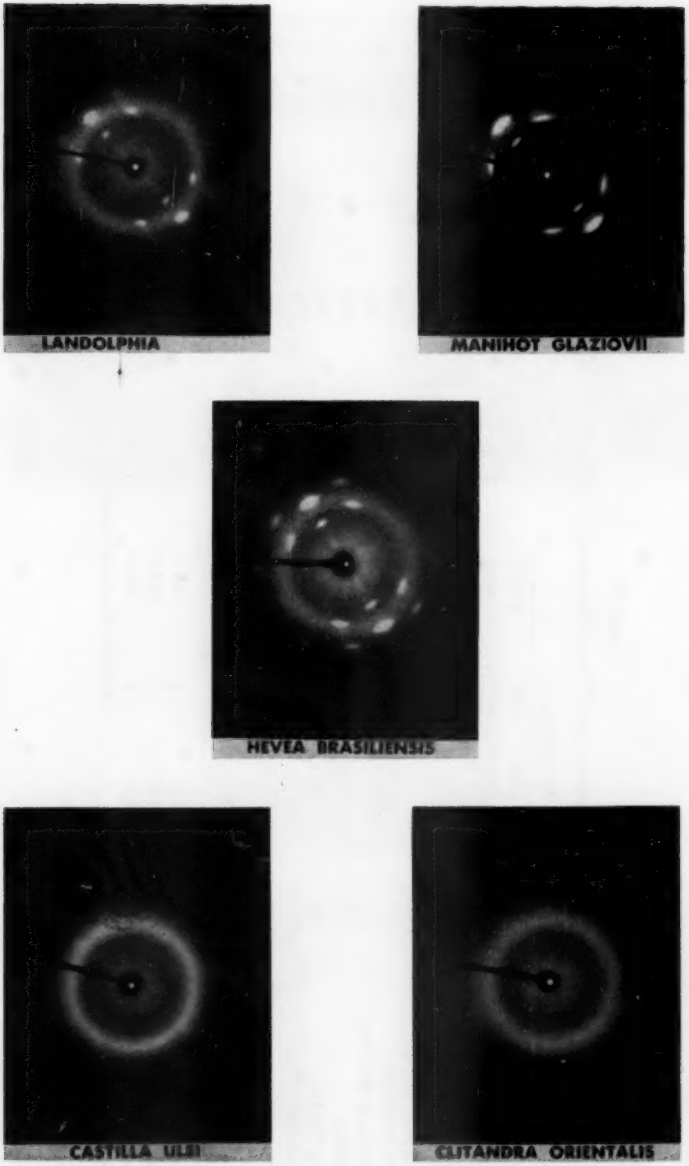

FIG. 3.—X-ray diffraction patterns of polymers.

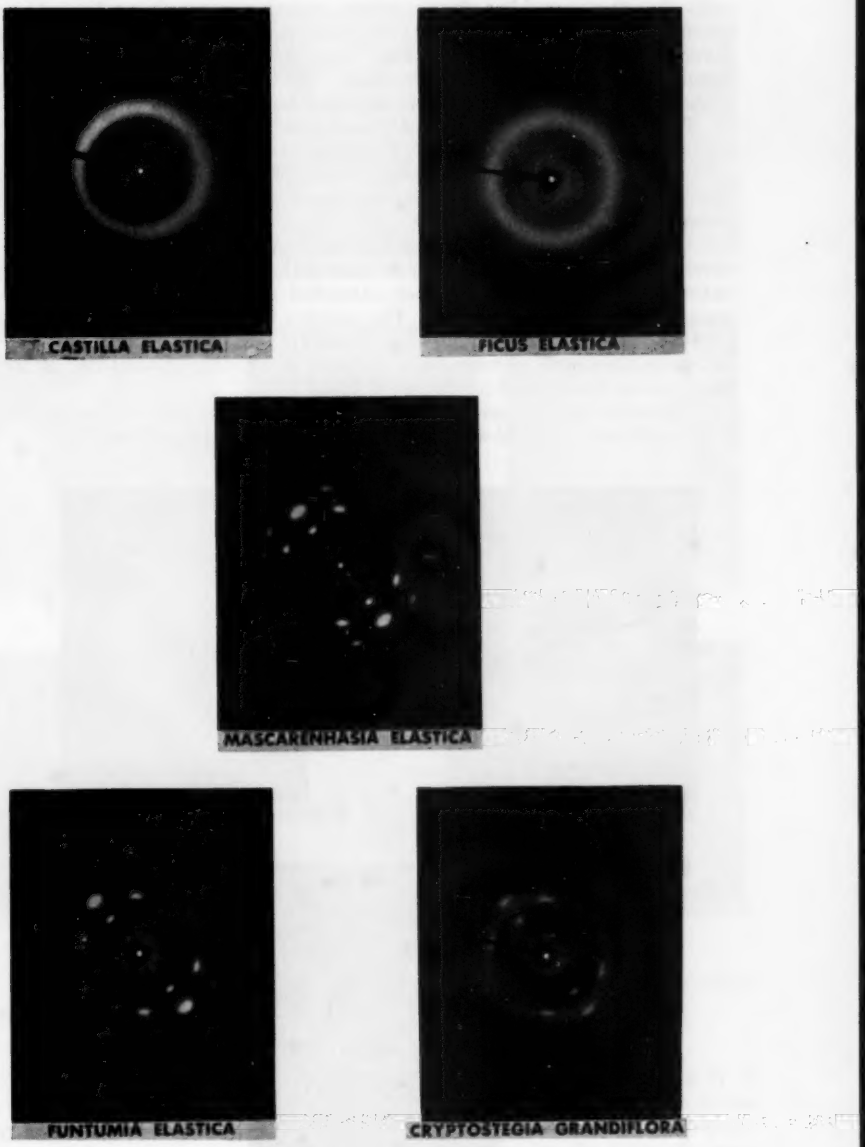

FIG. 4.—X-ray diffraction patterns of polymers.

cally changing the acid or alkali solution, until the aqueous layer did not become colored. The aqueous layer was then separated and the polymer in the toluene layer coagulated in acetone. The coagulated polymer was redissolved in toluene and again coagulated in acetone. The polymers were then dried under high vacuum and carbon disulfide solutions were prepared.

The microstructures of the polymers were determined by the method described by Binder and Ransaw[5]. The results are given in Table II. There was an insufficient amount of Pallaquium philippinensis to purify for the microstructure determination but an infrared spectrum was obtained and the polymer found to be *trans*-1,4.

X-ray diffraction photographs were made with the same samples used for determining the microstructures. Films of the polymers were rolled into cylinders about $\frac{3}{32}$ inch in diameter, stretched at room temperature and then quenched in a bath at −70° C. The samples were maintained at dry-ice temperature while the x-ray photographs were made. The results of the x-ray determinations are also recorded in Table II and photographs of the diffraction patterns are reproduced in Figures 3, 4 and 5.

Inherent viscosity and gel determinations of the coagulated polymers, for which sufficient material was available, are also reported in Table II.

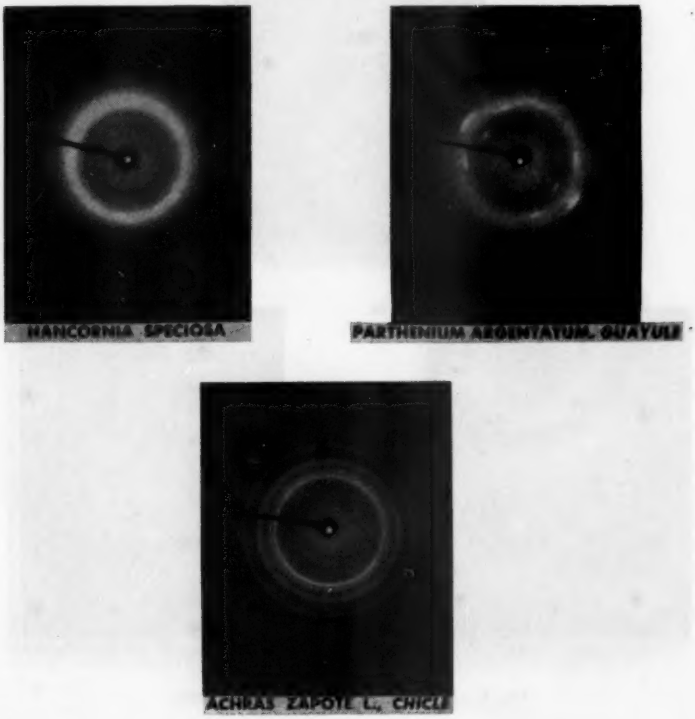

FIG. 5.—X-ray diffraction patterns of polymers.

FIG. 6.—Photographs of plants.

Pictures of many of the plants which are the sources of the rubbers studied here are shown in Figure 6.

DISCUSSION

Considering the variety of plants represented by the samples in Table II, it is indeed impressive that most of them have the same microstructures as Hevea (97.8% *cis*-1,4; 2.2% 3,4). This raises the question whether all of these polyisoprenes have the same precursors and are produced by the same enzymes, especially since the isoprenoid structure is widely distributed in natural products even though they are not all rubbers. In the case of the rubbers reported here the similar stereospecificities may indicate common precursors and

reaction mechanisms but different enzymes, one which forms the *cis* structure and another the *trans*. Then, for Chicle, two enzymes would be present in the plant. While recent discoveries[3, 6] have led to the production of stereospecific polyisoprenes in organic solvents, the elusive objective of making such polyisoprenes in aqueous media, as the plant does, remains to be attained.

The results in Table II show differences in the degree or amount of crystallinity for different samples. Whether these are real or due to the purification procedure is not known for certain. In the case of Guayule, it is known that the deproteinized sample used for the microstructure determination did not give a crystalline x-ray pattern. The sample used for the x-ray measurements reported here was not deproteinized, simply resin free. Unfortunately sufficient amounts of the samples in question were not available to determine whether this would be true for all.

ACKNOWLEDGMENTS

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DETERMINATION OF LATEX PARTICLE SIZE DISTRIBUTIONS BY FRACTIONAL CREAMING WITH SODIUM ALGINATE *

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Knowledge of mass distribution of particle sizes in latex is very important to the latex technologist. Therefore, it is desirable to have available a simple method for the determination of mass distribution of particle sizes. This paper presents a method, based on fractional creaming of latex with sodium alginate, which can be used in any laboratory without special equipment. The method is particularly advantageous for analyzing latexes of very wide particle size distributions. When analyzed with an electron microscope, these latexes require counting a very large number of particles.

McGavack[3] found that partial creaming of normal hevea latex with ammonium alginate gives concentrates of larger average particle size than the original latex. He found that the average particle size in the cream approaches that of the original latex as the amount of creaming agent is increased. In a previous paper from this laboratory, Schmidt and Kelsey[4] demonstrated that the phenomenon of fractionation according to particle size with increasing amounts of creaming agent is applicable in a wide variety of anionic latex systems and in colloidal silica. Their results indicated also the existence of a quantitative relationship, independent of the nature of the dispersed particles, between the concentration of creaming agent and size of creamed particles. Maron[2] confirmed fractionation with respect to particle size as a consequence of partial creaming with alginate. He showed that the mass average particle sizes of fractions, determined optically, cumulate to that of the original latex.

Although the previous paper by Schmidt and Kelsey[4] implied the basic concept of a method of determining particle size distribution by fractional creaming, it was not exploited at that time. In order to adapt the fractional creaming phenomenon to a quantitative method for particle size determination, we required a more precise knowledge of the relation between creaming agent concentration and size of particles creamed. It was proposed to establish this relationship with the aid of the electron microscope. Various factors influencing the creaming of latex, such as polymer concentration, electrolyte, soap content, and variability of the creaming agent, had to be considered in standardizing the creaming procedure.

DEFINITIONS AND MATERIALS

1. *Polymer content*: actual polymer plus adsorbed soap.
2. *Aqueous phase*: total system minus the polymer content.

* Presented at the September, 1960, meeting of the Division of Rubber Chemistry ACS. Also published in *Rubber Age* **88**, 484 (1960).

3. *Cream*: that portion of the polymer comprising particles of diameter equal to, or greater than, the minimum size which can be creamed by the prevailing concentration of creaming agent under the conditions of the experiment.

4 *Skim*: the entire system minus the cream.

It will be noted that these definitions of cream and skim differ from the usual concept of a cream layer and a skim layer[5]. The definitions of cream and skim adopted here are unambiguous and lend themselves to the simple mathematical treatment employed, for which all of the required information is obtained from analysis of the skim.

The following materials were used: sodium alginate (Kelcosol from the Kelco Company), of viscosity approximately 15 cp in 0.1 per cent aqueous solution at 25° C; the viscometer was a Kimble size 200 Fenske type. The

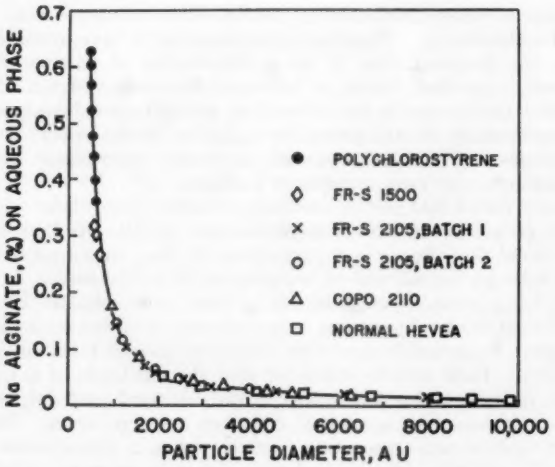

FIG. 1.—Calibration of sodium alginate concentration against latex particle size.

viscosity was 31.5 cp when measured with a Model LVF Brookfield Number 1 spindle at 60 revolutions a minute. Sodium pentachlorphenate (Santobrite Powder from Monsanto Chemical Co.). Dialyzer tubing ($1\frac{1}{8}$ inch diameter cellophane). Potassium oleate, 20 per cent solution.

EXPERIMENTAL PROCEDURE

(1) A stock solution of fresh sodium alginate was prepared containing 1 per cent alginate and 0.1 per cent sodium pentachlorphenate. Allowance was made for the moisture content of the Kelcosol, which runs about 8 to 12 per cent of the commercial product. It is advisable to determine the total solids of the final solution. This creaming agent solution was kept under refrigeration when not in use, and made up fresh after about a month.

(2) To a quantity of latex containing 100 grams of latex solids were added 4.0 grams of potassium oleate as a 20 per cent solution, and enough distilled water to make a total of 1000 grams of nominally 10 per cent latex. This mixture was analyzed for total solids, and the concentration of latex solids was calculated from the known soap content and the total solids.

TABLE I

FRACTIONAL CREAMING OF LATEX FR-S 2105. BATCH II WITH KELCOSOL (CONSTANT POLYMER CONTENT)

			Number of Creaming Mix										
			1	2	3	4	5	6	7	8	9	10	11
Latex FR-S 2105, Batch II, 62.5% T.S.	167	grams											
K-Oleate 20%	20	grams											
Distilled H_2O	813	grams											
"10%" Latex Stock Solution	1000	grams	50	50	50	50	50	50	50	50	50	50	50
Per cent T.S. of "10%" Latex Stock Solution	10.84												
Per cent Latex Solids of "10%" Stock Solution	10.44												
Kelcosol solution 0.885% (grams)*			3.9	5.8	7.9	10.5	15.7	19.5	22.5	24.7	26.4	31.2	39.0
Distilled H_2O (grams)			146.1	144.2	142.1	139.5	134.3	130.5	127.5	125.3	123.6	118.8	110.0
S_s: Solids of Skim (weight fraction $\times 10^2$)			2.524	2.448	2.378	2.274	2.042	1.752	1.447	1.212	1.083	0.689	0.510
C_{pm}: Polymer in Mix Prior to Creaming (weight fraction $\times 10^2$)			2.475	2.475	2.475	2.475	2.475	2.475	2.475	2.475	2.475	2.475	2.475
C_{ps} Polymer in Skim (weight fraction $\times 10^2$)			2.27	2.19	2.11	1.99	1.74	1.42	1.10	0.85	0.72	0.30	0.08
M_s: Mass Fraction of Polymer Remaining in Skim $\times 10^2$			91.7	88.1	84.7	80.0	69.5	56.8	43.8	33.9	28.4	11.7	3.03
C_k: Kelcosol Concentration on Aqueous Phase (weight fraction $\times 10^2$)			0.0178	0.0264	0.0360	0.0479	0.0716	0.0889	0.103	0.113	0.121	0.142	0.178
C_{sb}: Santobrite Concentration on Aqueous Phase (weight fraction $\times 10^2$)			0.0018	0.0027	0.0036	0.0048	0.0071	0.0089	0.010	0.011	0.012	0.014	0.018
C_{uf}: Concentration of Ultrafiltrate (weight fraction of aqueous phase $\times 10^2$)			0.136	0.136	0.136	0.136	0.136	0.136	0.136	0.136	0.136	0.136	0.136
C_s: Concentration of Added Soap (weight fraction of aqueous phase $\times 10^2$)			0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103

* Containing 0.088% Santobrite.

(3) A number of mixtures was prepared containing a constant amount of latex solids and varying amounts of sodium alginate, by mixing thoroughly 50 gram portions of the above soap stabilized 10 per cent latex with the desired amounts of the sodium alginate solution and enough distilled water to make 200 grams of mixture. The quantities of sodium alginate to be used depend on the particle size at which it is desired to make the separation. The required concentrations of alginate may be taken from Figure 1 or Table II. Representative examples of the data involved in a creaming series are shown in Table I. The number of mixtures required will depend on the precision with which it is desired to determine the distribution. In most cases about 10 mixtures are sufficient, but for routine control work this number can be reduced.

(4) The various, well stirred, latex mixtures were immediately poured into separatory funnels of appropriate size and allowed to cream at room temperature for 24 to 48 hours.

(5) The polymer content of the mixtures was determined from the following relationship:

$$C_{pm} = \frac{S_m - (C_s + C_{uf})}{1 - (C_s + C_{uf})} \tag{1}$$

This method of calculating polymer content was used in preference to a direct determination of polymer content because of its convenience.

C_{pm} = polymer concentration of the mix (weight fraction of the mix).
C_s = concentration of added soap (weight fraction of the aqueous phase).
C_{uf} = concentration of the ultrafiltrate solids (weight fraction of the aqueous phase).
S_m = one fourth of the total solids concentration of the 10 per cent latex stock solution, and represents the total solids of a creaming mixture prepared without any alginate (weight fraction of mix).

The weight of aqueous phase in a given weight of creaming mix is equal to:

$$\frac{\text{weight of mix} - \text{weight of latex solids in the mix}}{1 - C_{uf}}$$

The weight of latex solids is obtained from the previously calculated latex solids content of the 10 per cent latex stock solution. The weight of aqueous phase is constant for all mixes, but the composition varies.

In practice, a negligible error is committed if the denominator above is set equal to 1.0.

The ultrafiltrate was obtained from a portion of the original latex diluted without added soap to a latex solids equal to one fourth that of the 10 per cent latex stock solution. About 500 grams of this diluted latex was placed in a well washed and dried dialysis tubing which was then hung in a closed container. The ultrafiltrate was allowed to collect in the bottom of the container simply by the hydrostatic pressure of the latex in the tubing. By the time the creaming operation was finished, sufficient ultrafiltrate had collected to allow determination of its solids content (C_{uf}). Any turbidity in the ultrafiltrate indicates leakage and the collection of ultrafiltrate must be repeated.

(6) After the mixtures had been allowed to cream for 24 to 48 hours, the skim fractions were analyzed for total solids. The first few drops of skim, withdrawn from the bottom of the separatory funnel, were discarded and the major portion of the skim was withdrawn for solids determination, leaving behind

enough skim to avoid contamination of the sample with cream. The polymer concentrations of the skim portions were calculated from the relation:

$$C_{ps} = \frac{S_s - (C_s + C_{uf} + C_{sa} + C_k)}{1 - (C_s + C_{uf} + C_{sa} + C_k)} \tag{2}$$

where

C_{ps} = polymer concentration of skim (weight fraction of skim).
S_s = solids concentration of skim (weight fraction of skim).
C_{sa} = Santobrite concentration (weight fraction of aqueous phase).
C_k = Kelcosol concentration (weight fraction of aqueous phase) and the others are as previously defined.

(7) The weight fraction of the total polymer remaining in the skim of each mixture was calculated from the relation:

$$M_s = \frac{C_{ps}}{C_{pm}} \times \frac{1 - C_{pm}}{1 - C_{ps}} \tag{3}$$

M_s = fraction of the polymer remaining in the skim, and therefore the fraction of the polymer below a critical particle size corresponding to the creaming agent concentration.

(8) The cumulative mass distribution of particle sizes (Figures 5, 6) was obtained by plotting M_s against the particle diameters corresponding to the alginate concentrations used. These diameters are obtained from the calibration curve in Figure 1. To avoid the difficulty of accurately reading Figure 1,

TABLE II

CALIBRATION OF SODIUM ALGINATE CONCENTRATION AGAINST PARTICLE SIZE

Particle diameter, Angstrom units	Sodium alginate concentration (% aq. phase)	Particle diameter, Angstrom units	Sodium alginate concentration (% aq. phase)
500	0.525	2,200	0.0545
550	0.415	2,400	0.0490
600	0.310	2,600	0.0450
650	0.285	2,800	0.0410
700	0.265	3,000	0.0375
750	9.235	3,200	0.0350
800	0.220	3,400	0.0335
850	0.195	3,600	0.0320
900	0.185	3,800	0.0305
950	0.170	4,000	0.0290
1000	0.160	4,250	0.0275
1100	0.135	4,500	0.0255
1200	0.118	4,750	0.0240
1300	0.105	5,000	0.0225
1400	0.0945	5,500	0.0215
1500	0.0860	6,000	0.0195
1600	0.0780	6,500	0.0180
1700	0.0730	7,000	0.0170
1800	0.0680	7,500	0.0160
1900	0.0640	8,000	0.0150
2000	0.0610	9,000	0.0130
		10,000	0.0110

the alginate concentration for selected values of particle size are tabulated in Table II. In practice, the data in Table II can be used to construct a graph on an adequate scale or one can interpolate linearly between adjacent values.

THE CALIBRATION CURVE

The calibration curve in Figure 1 was constructed from mass-particle size distributions determined by the electron microscope, and fractional creaming curves obtained on each of five widely different latexes. The fractional creaming curves, illustrated in Figure 2, were obtained by plotting M_s as calculated above against sodium alginate concentration. The latexes used were normal hevea latex, Copo S-2110 latex, two batches of FR-S 2105, an FR-S 1500 type latex and a polychlorostyrene latex. The ability of fractional creaming to distinguish between latexes is apparent in these curves. Each of the first three of these latexes, as shown in Figure 4, covers a wide range of particle sizes.

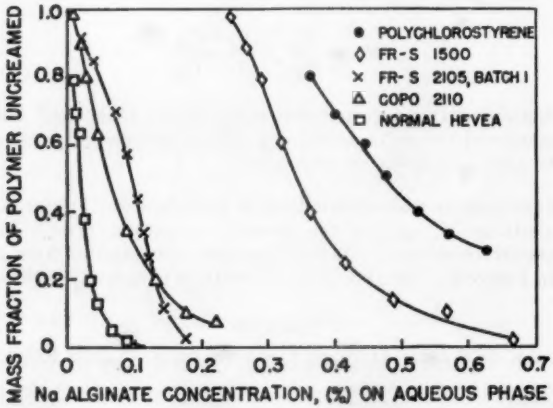

FIG. 2.—Fractional creaming of calibration latexes.

The electron microscope determination of mass distribution of particle sizes, in latexes having a wide distribution of sizes, is subject to large sampling errors. To reduce the sampling error, each latex was divided into a series of relatively narrow fractions so that each fraction could be accurately analyzed with the electron microscope. This fractionation was performed by means of an incremental creaming operation, in which a large volume of dilute latex (2.5 per cent solids) was treated with a small amount of creaming agent. The cream layer was removed and another increment of creaming agent was added to the skim to produce a second cream fraction. This process was repeated until the final skim contained only a small portion of the total polymer. The fraction of the total polymer creamed by each increment of sodium alginate is equal to $1\text{-}M_s$. M_s was determined from Equation III, with the requirement that C_{pm} for each fractionation corresponds to C_{po} from the previous fractionation. Correction was made for the small dilution by the incremental amount of creaming agent solution added.

The frequency distributions of particle sizes in each cream fraction and the final skim were determined with the electron microscope and the histogram

plotter described by Kelsey and Hanson[1]. A correction for bromination of the latex particles was applied to all latexes except polychlorostyrene by reducing the diameter 9.6 per cent. The number of particles counted varied from fraction to fraction, but the total for a given latex was in the vicinity of 3000 particles. Because of the advantage gained by fractionation, this number was considered adequate for reasonable accuracy. The frequency distributions for the fractions were each converted to mass distributions, which were then weighted according to the proportion of total polymer present in each fraction. The weighted mass distributions were summed over the latex fractions to produce the mass distribution for the whole latex. Cumulation of this distribution over the size groups gives the cumulative mass distribution of the whole latex. Figure 3 shows the cumulative mass distributions of particle sizes in

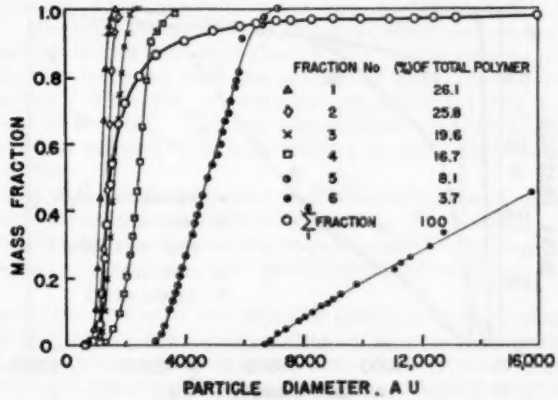

FIG. 3.—Cumulative mass distribution of particle sizes in fractions of 2105 latex, batch 2, and their summation.

each fraction of FR-S 2105 batch 2, and the resulting cumulative distribution for the whole latex. Cumulative mass distributions of particle sizes for each of the calibration latexes are shown in Figure 4.

The procedure for calculating the cumulative mass distribution of particle sizes from electron microscope examination of fractions is expressed formally:

i = the particle size group number, and assumes integral values from 1 to k.
j = the latex fraction number, and assumes integral values from 1 to n.
P_{ij} = the number of particles in the ith group of the jth fraction.
F_j = the weight fraction of the total polymer residing in the jth fraction.

The fraction of the total mass residing in the ith particle size group is then found by calculating

$$\sum_{j=1}^{n}\left[\frac{i^3P_{ij}F_j}{\sum_{i=1}^{k}}\right]i^3P_{ij}\text{K}$$

Plotting the cumulative values of this expression for each value of i against particle size gives the cumulative mass distribution of particle sizes in the latex.

The particle size is equal to $i \times d$ where d is the size of the group interval in Angstrom Units (A).

Data used in constructing the calibration curve of Figure 1 were obtained by determining alginate concentration and particle size corresponding to numerically equal values of weight fraction of polymer in a given latex from the curves of Figures 2 and 4.

Application of these procedures to each of the calibration latexes provided overlapping portions of the calibration curve. The fact that the data from such a variety of latexes, as used in this calibration, fall on a smooth curve lends weight to the necessary assumption that a given concentration of creaming agent creams substantially those particles which are above a certain size, regardless of the nature of the latex.

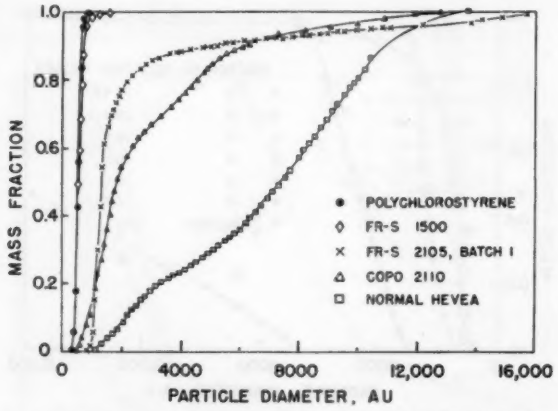

FIG. 4.—Cumulative mass distribution of particle sizes in calibration latexes.

If particle size is plotted against the reciprocal concentration of alginate, the calibration curve can be approximated by a straight line defined by the expression $D = 223 + 111.7\ (1/C)$ where D = particle diameter in A, and C = alginate concentration in per cent on the aqueous phase.

This expression can be used instead of the calibration curve for estimating particle size, but with some loss of accuracy at the small particle end of the range.

DISCUSSION

The experimental variables expected to affect the relation between particle size and creaming agent concentration are:

1 Concentration of latex mixture.
2 Electrolyte concentration and pH.
3 Soap concentration.
4 Creaming time.
5 Properties of creaming agent solution.

Investigation of these factors indicated that the concentration of the latex prior to creaming did influence the creaming. This behavior was indicated

previously by Schmidt and Kelsey[4]. The magnitude of this effect decreases with decreasing latex concentration, and becomes acceptably small for concentrations of 2.5 per cent or less. The choice of 2.5 per cent latex solids as a standard concentration for fractional creaming is based on this observation.

Furthermore, effects of possible adsorption phenomena on concentration of the aqueous phase may be expected to be small at low polymer concentrations. Adsorption effects are assumed to be negligible in our treatment of the data. A lower concentration would have been advisable on theoretical grounds, but would have possibly complicated the determination of polymer content of the skim, because of the low ratio of polymer to non-polymer solids.

The effects of electrolyte content and pH were found sufficiently small so that variation in these factors, normally occurring in latex, had no significant effect on creaming. This observation has been confirmed in this laboratory by Adams[6]. However, the addition of buffers or other electrolytes should be avoided, since salt concentrations of about 0.02 *N* on the aqueous phase of the creaming mixture begin to shift the calculated distribution curve toward smaller diameter. When this concentration reaches about 0.05 *N*, the error becomes about 10 per cent. This salt concentration (Na_2HPO_4) represents a salt content of nine per cent of the latex solids, a quantity which is not likely to be met in practice.

The purpose of the soap added prior to dilution is to prevent coagulation on dilution, and to enhance the stability of the cream. The quantity of soap was found not to affect the creaming until a soap concentration of twenty parts per hundred polymer was reached, a level much higher than any likely to be met in practice.

The concentration of skim was found to remain essentially constant with time, despite the fact that the volume of the skim layer increases with creaming time. As a consequence, creaming time is not critical, provided that sufficient time is allowed for accumulation of enough skim so that the 20 to 40 gram sample for solids determination can be obtained without disturbing the boundary. Because of the high viscosity associated with high alginate concentrations, the time required under these conditions is greater than for low alginate concentrations. In any case, a minimum of 24 hours should be allowed for creaming. Creaming with alginate has been accelerated in a centrifuge by Maron[2] but this method was not used.

The nature of the sodium alginate employed as creaming agent is very important. Alginate solutions undergo bacterial decomposition on aging and creaming efficiency decreases as the alginate becomes degraded. Therefore, preservation with sodium pentachlorphenate was adopted as standard practice. The preservative was found to introduce no significant effects of its own. The use of preservative, and storage of the solution under refrigeration, maintained constant creaming characteristics of the alginate for a period of at least one month. A decrease in viscosity of the alginate solution indicated decomposition, although a decrease of as much as sixteen per cent had no significant effect on the creaming. Two batches of Kelcosol were observed to differ 5 per cent in initial viscosity without affecting the creaming results.

A variety of materials other than alginates are known creaming agents for latex, but the quantities required to produce the same effects vary with the nature of the material. Consequently, their use would necessitate the determination of a new calibration curve for each material.

Sodium alginate was selected because it is relatively efficient, and in contrast to the ammonium salt, it avoids the volatile base which affects the cal-

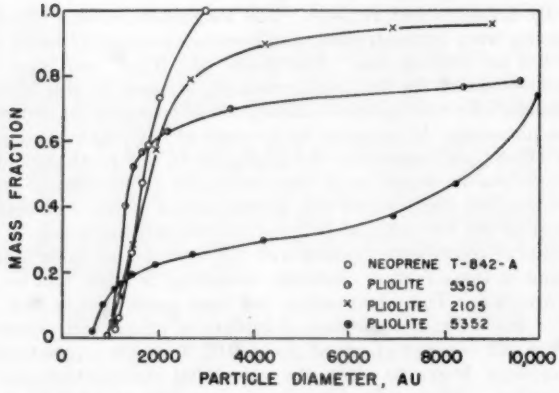

FIG. 5.—Cumulative mass distribution of particle sizes in current synthetic latexes.

culation of polymer content. Furthermore, it is available in a refined grade for food and pharmaceutical uses.

The procedure for determining mass distribution of particle sizes in latex by fractional creaming has been applied to a number of latexes of widely different characteristics, containing a variety of polymer types. Cumulative distribution curves for Pliolite 2105, Pliolite 5352, Pliolite 5350, Neoprene T-842A, FR-S 168, FR-S 200, and a butadiene/vinyl pyridine copolymer latex (Bd/VP.) latex are shown in Figures 5 and 6. All but the last are commercially available. The points lie on smooth curves, covering a range of particle sizes from 500 to 10,000 A. This represents the useful limits of the calibration curve. The extreme differences between the mass distributions are quite obvious, and should help account for some of the observed characteristics of the latexes.

In Pliolite 5350 and 5352, a substantial portion of the mass comprises particles which exceed in size the upper limit of the method described here. Al-

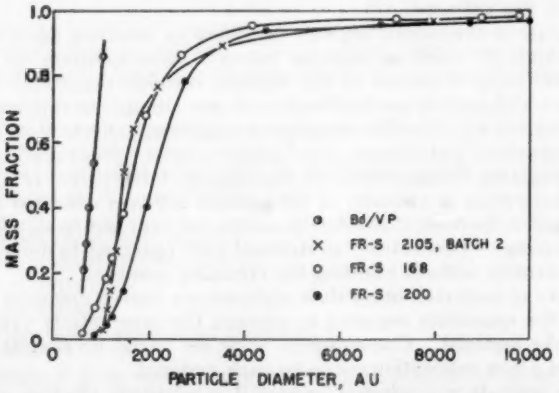

FIG. 6.—Cumulative mass distribution of particle sizes in current synthetic latexes.

though the curves for these latexes give the distribution of only that portion of the mass below 10,000 A they do determine quantitatively the mass of polymer above 10,000 A. Because of the low frequency of large particles in such latexes of very wide particle size distribution, methods which depend on particle counting may give very inaccurate estimates of the mass in large particles, unless a very large number of particles is counted. If the mass in particles larger than a given size is uncertain, the distribution for particles below that size will be correspondingly uncertain. If the distribution above 10,000 A is desired, another method is called for.

While the major objective of this paper is to present a method for determining mass distribution of particle sizes without the use of expensive equipment, it should be mentioned that if an electron microscope is available good use can be made of the incremental creaming procedure. This will greatly improve analysis of latexes with wide distributions of particle sizes. An example is latex FR-S 2105 batch 1. Table III indicates the relative frequency of

TABLE III

COMPARISON OF NUMBER AND MASS DISTRIBUTIONS OF PARTICLE SIZES IN SBR (FR-S) 2105

Particle diameter, Angstrom units	Cumulative mass of polymer above size indicated (%)	Cumulative no. of particles above size indicated (%)	Probability of occurrence of particles larger than size indicated
1,000	94.0	85.0	0.85
1,500	38.9	9.4	0.094
2,000	24.3	1.87	0.019
3,000	15.9	0.25	0.0025
4,000	13.07	0.102	0.0010
5,000	11.14	0.045	0.00045
6,000	10.1	0.025	0.00025
10,000	6.4	0.006	0.00006
18,000	0	0	0

DERIVATION OF EQUATIONS

Polymer concentrations

Let: C_{pm} = concentration of polymer in creaming mixture (weight fraction of mix)

C_{ps} = concentration of polymer in skim (weight fraction of skim)

S_s = total solids of skim (weight fraction of skim)

S_m = total solids of mix (weight fraction of mix)

C_{aq} = concentration of solids in aqueous phase (weight fraction of aq. phase.)

$C_{aq} = (C_s + C_{uf} + C_{os} + C_k)$ where

C_s = concentration of added soap,

C_{uf} = concentration of ultrafiltrate,

C_{os} = concentration of Santobrite added in the Kelcosol, and

C_k = concentration of Kelcosol, all expressed as weight fractions of the aqueous phase of the total mixture.

By definition $(1 - C_{pm})$ represents the amount of aqueous phase expressed as wt. fraction of the total mix.

Then: $C_{pm} = S_m - (1 - C_{pm})\ (C_{aq})$

rearranging:

$$C_{pm} = S_m - C_{aq} + C_{pm}\,C_{aq}$$

$$C_{pm}\,(1 - C_{aq}) = S_m - C_{aq}$$

$$C_{pm} = \frac{S_m - C_{aq}}{1 - C_{aq}} = \frac{S_m - (C_s + C_{uf} + C_{ca} + C_k)}{1 - (C_s + C_{uf} + C_{ca} + C_k)}$$

If the S_m is determined on a sample prepared with no creaming agent, (as is preferred)

then C_{ca} and C_k are zero, and $C_{pm} = \dfrac{S_m - (C_s + C_{uf})}{1 - (C_s + C_{uf})}$ (I)

Similarly:

$$C_{ps} = S_s - (1 - C_{ps})(C_{aq})$$

$$C_{ps} = S_s - C_{aq} + C_{ps}\,C_{aq}$$

$$C_{ps}(1 - C_{aq}) = S_s - C_{aq}$$

$$C_{ps} = \frac{S_s - C_{aq}}{1 - C_{aq}} = \frac{S_s - (C_s + C_{uf} + C_{ca} + C_k)}{1 - (C_s + C_{uf} + C_{ca} + C_k)} \qquad \text{(II)}$$

where S_s is determined on the skim, and C_{ca} and C_k can not be zero. $(1 - C_{ps})$ is the aqueous phase expressed as weight fraction of the skim.

Mass fraction of polymer uncreamed

Let: W_m = weight of creaming mixture

W_{pm} = total weight of polymer

C_{pm} = concentration of polymer in mixture (weight fraction)

W_{pc} = weight of polymer creamed

W_s = weight of skim = $W_m - W_{pc}$ (by definition)

W_{ps} = weight of polymer in skim = weight of uncreamed polymer (by definition)

C_{ps} = concentration of polymer in skim (weight fraction)

$W_m - W_{pm}$ = weight of aqueous phase (by definition)

Then: $W_{pc} = W_{pm} - W_{ps}$

$$\frac{W_{ps}}{W_s} = \frac{W_{ps}}{W_m - W_{pc}} = C_{ps}$$

$$W_{ps} = C_{ps}\,(W_m - W_{pc}) = C_{ps}\,(W_m - W_{pm} + W_{ps})$$

$$W_{ps} = C_{ps}\,W_m - C_{ps}\,W_{pm} + C_{ps}\,W_{ps}$$

$$W_{ps} - C_{ps}\,W_{ps} = C_{ps}\,W_m - C_{ps}\,W_{pm}$$

$$W_{ps}\,(1 - C_{ps}) = C_{ps}\,(W_m - W_{pm})$$

$$W_{ps} = \frac{C_{ps}\,(W_m - W_{pm})}{1 - C_{ps}}$$

$$\frac{W_{ps}}{W_{pm}} = \frac{C_{ps}\,(W_m - W_{pm})}{W_{pm}\,(1 - C_{ps})}$$

$$\frac{W_{ps}}{W_{pm}} = \frac{C_{ps}\,(W_m - W_{pm})}{W_m\,C_{pm}\,(1 - C_{ps})} = \frac{C_{ps}\,W_m\,(1 - C_{pm})}{W_m\,C_{pm}\,(1 - C_{ps})} = \frac{C_{ps}\,(1 - C_{pm})}{C_{pm}\,(1 - C_{ps})}$$

Therefore, the uncreamed polymer M_s (as a weight fraction of the total polymer) is given by:

$$M_s = \frac{W_{ps}}{W_{pm}} = \frac{C_{ps}}{C_{pm}} \times \frac{(1 - C_{pm})}{(1 - C_{ps})} \qquad \text{(III)}$$

occurrence of particles of various sizes. Ten per cent of the mass occurs in particles over 6000 A, but the probability of finding a particle larger than 6000 A in a single observation is 0.00025 when examining the unfractionated latex. If the large particles are isolated and concentrated by fractional creaming, the mass distribution of these large particles can be determined satisfactorily by counting a few hundred particles. The upper end of the mass distribution curve thus can be based on a particle count that contains almost the same number of particles as other portions of the curve. Attainment of equivalent representation of large particle sizes in unfractionated latex requires counting many more particles.

Although this paper deals with mass rather than number distributions of particles sizes, the number distribution can be calculated once the mass distribution is known. Therefore, the method described here should be of use to those engaged in research on the theory of emulsion polymerization as well as to the latex technologist.

It is the hope of the authors that use of these procedures will make available to a greater number of laboratories the acquisition of particle size data which might be of value in the study of many latex problems.

SYNOPSIS

A method was developed for the determination of the mass distribution of particle sizes in latex, by fractional creaming with sodium alginate. This method was based on the observation that the size of creamed latex particles depends quantitatively on the prevailing concentration of sodium alginate, regardless of the nature of the latex. A calibration curve indicating inverse proportionality between creaming agent concentration and size of particles creamed was prepared with the aid of the electron microscope. By the use of this calibrat on curve particle size distributions of latexes over a range from 500 to 10,000 Angstrom units diameter can be determined with no equipment other than an analytical balance and a number of separatory funnels. This method is particularly advantageous for analyzing latexes of very wide particle size distributions, which, when examined with an electron microscope would require the counting of a very large number of particles. Detailed procedures and applications of this method are described.

ACKNOWLEDGMENTS

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LIGHT-SCATTERING MEASUREMENTS ON SOLUTIONS OF NATURAL AND SYNTHETIC POLYISOPRENES *

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INTRODUCTION

Comparatively few studies have been published on the light-scattering behavior of solutions of natural rubber[1-4], and these have been concerned with evaluating the intrinsic molecular properties of the polyisoprene chain. For this purpose it is necessary to remove from the solution under examination all other molecular species and especially those of great size (branched or crosslinked structures, colloidal debris, etc.). Structures of the latter type, for example microgel[5, 6], may influence the general properties of rubber, and it is undoubtedly the case that, for many purposes, *all* the components of a rubber solution, other than adventitious dirt, are potentially of interest. This is the standpoint of the present communication, in which are described light-scattering measurements on rubber solutions which have been clarified by filtration rather than by ultracentrifugation (which would remove some or all of the larger species present). Included for comparison is a study of a synthetic *cis*-1,4-polyisoprene, whose behavior was expected to be simpler than that of natural rubber.

EXPERIMENTAL

MATERIALS

Solvents were of Analar or reagent grade, distilled where appropriate.

Two samples of natural rubber were used (*1*) an unmilled pale crepe, and (*2*) a well-milled pale crepe. The sample of synthetic *cis*-1,4-polyisoprene was obtained from the Shell Development Co.

CLARIFICATION PROCEDURE

In conformity with the views expressed in the introductory paragraph, all solutions were clarified by filtration through sintered glass filters. The finest available—Grade 5 (Pyrex)—has a mean pore size of less than 2μ. Rubber solutions will not normally pass through a grade 5 filter unless they have been previously filtered through coarser filters. The standard procedure was to pass the solution in turn through filters of grades 3, 4, and 5 under 5–7 psi nitrogen pressure. In several cases extreme difficulty was experienced, and the filters blocked frequently. Once each solution had been put through a grade 5 filter, subsequent passages through this grade were rapid. Concentrations were determined after filtration by evaporating aliquots and heating *in vacuo* to constant weight. Dilutions were performed as appropriate.

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MEASUREMENTS

Turbidity measurements were carried out with a Brice-Phoenix Series 1000 photometer, using a small (15 ml) cylindrical cell with plane end-windows. The wavelength employed was 4358 A. The calibration data provided by the manufacturers were checked by measuring the 90° turbidity from a 0.5% solution in toluene of standard polystyrene[7]. The standard value for this sample is given as 3.51×10^{-3} cm^{-1}. Six separate measurements over a period of months gave, as an average, precisely this figure with a standard deviation of 0.06, i.e., less than 2%. Measurements of the Rayleigh ratio for purified benzene gave a mean value of 49.5×10^{-6}, slightly higher than the often-quoted[8] values of 48.5×10^{-6}.

Measurements were normally carried out at 10° intervals from 30° to 100° or 120° and at a range of concentrations from about $3\text{–}5 \times 10^{-3}$ g/ml down to about one-tenth of this. The depolarization factor with unpolarized incident light for natural rubber in cyclohexane was found to be less than 2% and hence no correction was applied. For the refractive index increment the values found by Altgelt and Schulz[2–4] were used. For tetrahydrofuran an interpolation was made from their data.

TABLE I

RELATIVE TURBIDITIES

	Filter grade[a]		
	3	4	5
Milled natural rubber in chloroform	3.12	1.47	(1.0)
Milled natural rubber in hexane	1.18	1.09	(1.0)
Synthetic polyisoprene in chloroform	5.27	1.21	(1.0)
Synthetic polyisoprene in hexane	1.39	1.32	(1.0)
Polystyrene in chloroform	1.03	1.01	(1.0)

[a] The pore sizes quoted by the makers are: 20–30 μ (grade 3), 5–15 μ (grade 4), <2 μ (grade 5).

All data were evaluated by the Zimm diagram method in which c/τ is plotted against $Kc + \sin^2 \frac{1}{2}\theta$, where c is the concentration (in grams/milliliter), τ the turbidity, θ the angle of observation, and K is an arbitrary constant chosen to give a well-spaced array of points. The light-scattering parameters tabulated are weight-average molecular weight $\bar{M}_w$, second virial coefficient A_2, mean-square radius of gyration $\bar{S}_z^2$, and $(\bar{r}^2/\bar{M}_w)^{\frac{1}{2}}$, where $\bar{r}^2$, the mean-square end-to-end distance of the equivalent random coil, is equal to $6\bar{S}_z^2$.

RESULTS AND DISCUSSION

EFFECT OF FILTRATION

Useful qualitative information can be obtained from a study of the effect of filtration on polymer solutions. Table I lists the relative changes in turbidity (at $\theta = 120°$) produced by passing rubber solutions through sintered glass filters of decreasing pore size. Solute concentrations were about 2×10^{-3} g/ml, and the turbidities are referred to unity for the grade 5 filter. A polystyrene sample, included for comparison, shows negligible changes as the filtration severity is increased.

Concentrations were little affected by the filtration process. For the milled natural rubber in chloroform the decrease in concentration on proceeding from a grade 3 to a grade 5 filter was 7% and the corresponding decrease in intrinsic viscosity was only 5%. This is to be compared with a reduction in turbidity

of more than threefold (Table I). One can deduce from this that the material which is removed by filtration (possibly by an absorption process) is compact in shape, since it had little effect on viscosity. The sample of synthetic polyisoprene also contains a strongly scattering component. The decrements in turbidity when the rubbers are dissolved in the poor solvent hexane are much less. Only about half of each polymer sample is soluble in hexane, and the turbid component(s) is hence associated with that part of the polymer which is insoluble in hexane but dispersible in the good solvent chloroform. Since both the natural and synthetic polyisoprenes show these effects one cannot attribute them solely to those nonrubber components which are known to occur in natural rubber (proteins, etc.). It might be considered that in both rubbers there exist branched structures which can be in part removed by filtration.

TABLE II

SYNTHETIC *cis*-1,4-POLYISOPRENE

Mastication treatment	$[\eta]_{\phi CH_3}$	$[\eta]_\theta$	Solvent	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$, ml/g	$\bar{S}_z^2 \times 10^{15}$, A^2	$(\bar{r}_z^2/\bar{M}_w)^{\frac{1}{2}}$ $\times 10^{21}$
None	6.50	1.69	$CHCl_3$	16.8	8.2	9.20	1820
			THF	9.51	9.2	4.46	1680
			theta	10.75	—	2.36	1140
3 min in air	4.25	1.44	THF	6.52	8.0	3.00	1660
30 min in N_2	4.24	1.41	$CHCl_3$	14.5	6.1	6.47	1630
			THF	6.21	8.1	3.48	1830
60 min in N_2	3.98	1.42	THF	6.39	6.9	2.89	1650
10 min in air	3.00	0.95	$CHCl_3$	7.40	10.2	2.94	1540
			THF	4.45	7.0	2.14	1700
			theta	4.50	—	0.49	810
50 min in air	1.76	0.77	THF	2.61	12.3	0.88	1420

MEASUREMENTS WITH SYNTHETIC *cis*-1,4-POLYISOPRENE

Samples were masticated under various conditions and their light-scattering behavior examined in chloroform ($CHCl_3$), tetrahydrofuran (THF), and di-*n*-butyl ether/*n*-butanol 60/40 (theta). This last mixture is a near theta-point solvent for polyisoprene, and the refractive indices of the components are almost identical, as required[8]. Table II lists the results. With the exception of the data for chloroform, the light-scattering behavior of this polymer is regular. Molecular weights measured in a good solvent (tetrahydrofuran) and a near theta solvent are in close agreement.

Figure 1 shows $\log \bar{M}_w$ plotted against $\log [\eta]$, the relations being

$$[\eta]_{\phi CH_3} = 5.9 \times 10^{-6} \bar{M}_w^{1.01}$$

and

$$[\eta]_\theta = 3.0 \times 10^{-4} \bar{M}_w^{0.63}$$

The exponents are substantially greater than the theoretical maximum value of 0.8 and 0.5, respectively. Even higher values have been found for $\bar{M}_n$ vs. $[\eta]$ with masticated natural rubber and have been attributed to nonrandom chain fracture resulting in a progressive sharpening of the molecular weight distribution as mastication progresses[9].

The mastication of natural rubber in nitrogen, rather than in air, produces chain branching leading eventually to gel formation[10]. The data of Table II and Figure 1 do not reveal such an effect with the synthetic polyisoprenes, though the data are rather too limited to be decisive. Prolonged mastication

in nitrogen produced a little gel, but the Huggins k' values, obtained from the viscosity measurements, are reasonably constant[10].

The last column of Table II reveals that in tetrahydrofuran $\bar{r}^2$ is proportional to $\bar{M}_w$ and there is no variation in the quotient with manner or extent of mastication. This parameter is probably not very sensitive to structural changes. Although the quotient might be expected to decrease if branched structures are introduced, this effect may be swamped by alterations in the molecular weight distribution since $\bar{r}^2$ is a z-average and $\bar{M}$ a weight average. As expected, the quotient is diminished on passing from a good to a near theta-point solvent, as a result of the coiling-up of the polymer molecules. The mean value in the theta solvent (970×10^{-11}) is close to that (830×10^{-11}) derived by Wagner and Flory[11] from viscosity data. This is much higher than the theoretical figure (485×10^{-11}) computed for a polyisoprene chain with free rotation[12].

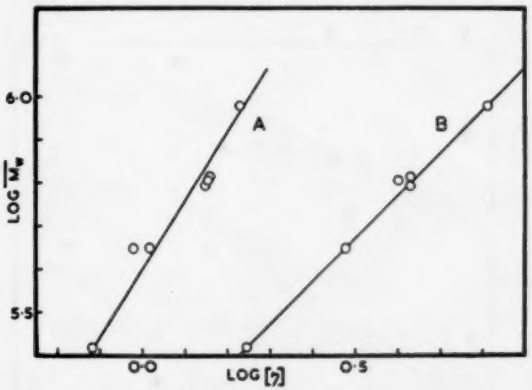

FIG. 1.—Relationship between $\bar{M}_w$ and intrinsic viscosity in (*A*) theta solvent mixture and (*B*) toluene for synthetic polyisoprenes.

For all these samples of synthetic polyisoprene the Zimm diagrams were regular with both the $c = 0$ and $\theta = 0$ lines being linear. In this region of molecular weight, curvature of the $c = 0$ line would not be expected unless the ratio $\bar{M}_w/\bar{M}_n$ is quite large. Some measurements of $\bar{M}_n$ for several of the samples indicated that the ratio was only about 1.5. Values of A_2, derived from the $\theta = 0$ lines, are typical of those for polymers in good solvents, but no very clear trends can be seen.

No convincing reasons can be put forward to explain the abnormally high values for $\bar{M}_w$ obtained using chloroform as solvent. It is clear from the filtration experiments (Table I) that chloroform solutions contain a highly scattering substance and it is very likely that, if more drastic filtration (or ultracentrifugation) could be employed, the values of $\bar{M}_w$ would approach those found with the other solvents.

MEASUREMENTS WITH UNMILLED NATURAL RUBBER

Altgelt and Schulz[2–4] have made extensive use of cyclohexane as a light-scattering solvent for natural rubber. In one respect it is a good choice, since it gives an acceptably large refractive index increment. But, despite the fact

that it is thermodynamically a good solvent for rubber, it is usually found that gel contents in cyclohexane are substantially higher than in, for example, benzene. The sample of unmilled pale crepe rubber used here was approximately 50% soluble in cyclohexane. Removal of the macrogel phase by filtration through lens tissue gave an apparently clear solution which could be filtered, with difficulty, through sintered glass filters.

Figure 2 shows the Zimm diagram obtained from the solution. It is very distorted, by contrast with diagrams obtained both with synthetic polyisoprene and with the milled crepe natural rubber. Distorted plots of this form are commonly ascribed to the presence of microgel[12–15], and a very similar plot for natural rubber in cyclohexane has been published by Altgelt and Schulz[3]. It is in principle possible to compute the size of the microgel particles from the curvature of the $c = 0$ line[3], provided that the molecular weight (and its distribution) of the linear macromolecules is known. One can attempt to obtain $\bar{M}_w$ by an extrapolation of the linear portion of the Zimm plot, and, from

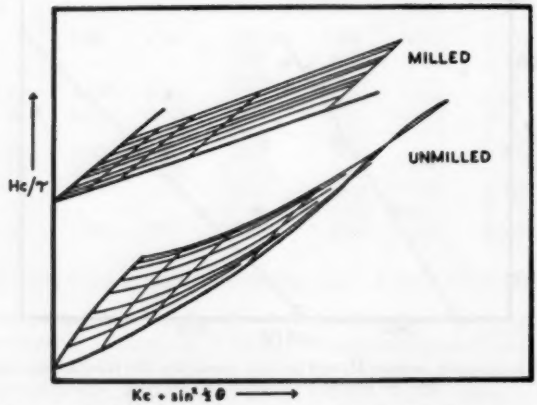

FIG. 2.—Zimm diagrams for milled and unmilled natural rubber in cyclohexane. For clarity the individual points are not shown and the ordinates are displaced.

Figure 2 a rough value of 1.4×10^6 is obtained, but this procedure is very subjective. By computing theoretical particle scattering factors for linear molecules and for spheres which scatter according to the Mie formula, Altgelt and Schulz estimated the diameter of the microgel particles to be around 5000 A. The existence of microgel in natural rubber has previously been demonstrated by other methods[5, 6] and is confirmed by the light-scattering method.

EFFECT OF SOLVENT

In order to investigate the effect of changing the solvent it is necessary to use a sample of natural rubber which is, as far as possible, fully soluble in all the solvents used, otherwise the results may be confused by fractional dissolution. For the experiment of this section, a well-milled pale crepe was employed. The choice of solvent is restricted to those whose refractive index increments are reasonably large and preferably greater than 0.1. Of the four solvents used here, three—chloroform, tetrahydrofuran, and the near-theta solvent (di-*n*-butyl ether/*n*-butanol 60/40)—dissolved virtually all the rubber, while in the

fourth—*n*-hexane—the rubber was only about 50% soluble. Table III lists the light-scattering data, together with the universal constant Φ given by[12]

$$\Phi = [\eta]\bar{M}_w/(\bar{r}^2)^{\frac{3}{2}}$$

where $[\eta]$ is the intrinsic viscosity in the same solvent.

In a further experiment a sample of the same rubber was separated into sol and gel fractions by dissolution in cyclohexane for 72 hours. The sol was recovered by freeze-drying and dissolved in tretahydrofuran for light-scattering measurements. The gel was dispersed in chloroform (Table IV).

TABLE III

MILLED NATURAL RUBBER

Solvent	$[\eta]$	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$, ml/g	$\bar{S}_z^2 \times 10^{13}$, A^2	$\left(\frac{\bar{r}^2}{\bar{M}_w}\right)^{\frac{1}{2}} \times 10^{11}$	$\Phi \times 10^{-21}$
Chloroform	3.13	19.6	~0	5.79	1330	0.95
Tetrahydrofuran	2.58	14.8	~0	4.12	1290	0.98
n-Hexane	2.20	7.8	2.8	2.17	1290	1.16
Theta solvent	0.92	4.4	0	0.97	1140	0.91

In these experiments the Zimm diagrams were quite regular, showing none of the distortion displayed by the unmilled rubber (Figure 2). A striking feature is that, as the solvent power of the solvent is increased, so $\bar{M}_w$ increases and A_2 tends to zero. It is likely that these two effects are interconnected. A consistent explanation is that the rubber contains a highly scattering component. The weight fraction of this component must be quite small, since the samples were virtually (~99%) soluble in three out of the four solvents used. Progressive solubilization of this component as the solvent power is increased would undoubtedly cause $\bar{M}_w$ to increase; it appears that it is also associated with abnormally low values of A_2. This component can be retained by the macrogel phase of the rubber which, when separated from the sol phase, actu-

TABLE IV

BEHAVIOR OF SOL AND GEL FRACTIONS

	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$, ml/g	$\bar{S}_z^2 \times 10^{13}$, A^2	$(\bar{r}^2/\bar{M}_w)^{\frac{1}{2}} \times 10^{11}$
Sol fraction in tetrahydrofuran	4.1	6.3	1.83	1640
Macrogel fraction in chloroform	19.5	(−0.8)	3.2	1000

ally exhibits a negative value of A_2 (Table IV). This rather unusual behavior could be taken to indicate dissociation of the structure on dilution, though this interpretation is uncertain.

The behavior shown in Table III is broadly in line with the filtration experiments (Table I). Both indicate the existence of compact, highly scattering components. Further evidence for these comes from the values of $(\bar{r}^2/\bar{M}_w)^{\frac{1}{2}}$. The ratio for this parameter between a good and a theta solvent gives[13] the molecular expansion factor α. For tetrahydrofuran, for example, natural rubber (Table III) gives $\alpha = 1.13$, while *cis*-1,4-polyisoprene (Table II) gives $\alpha \approx 1.5$. The former value is unreasonably low for a good solvent, while the latter is of the expected magnitude. Expressed in another way, $\bar{r}^2$ for natural rubber is lower than that of *cis*-1,4-polyisoprene of the same molecular weight. This could be attributed to the existence of branched structures which lower $\bar{r}^2$.

An alternative explanation of the effects of Tables III and IV is that it is

the progressive solubilization of nonrubber components which increases $\bar{M}_w$ and lowers A_2. It is not yet possible entirely to eliminate this possibility but a consideration of the last column of Table II suggests that it is probably not the true explanation. If nonrubber components were dissolved by chloroform, for example, but not by the theta solvent, one would expect $[\eta]$ and $\bar{M}_w$ (apparent) in chloroform to be increased by unrelated amounts. In fact, the computed values of the constant Φ (which connects $[\eta]$, $\bar{M}_w$, and $\bar{r}^2$) are remarkably constant. Strictly speaking Φ should only be calculated for polymer fractions, for which it is normally[12] $2.0–2.5 \times 10^{23}$. Heterogeneity will reduce this somewhat, and may perhaps account for the value found. A similar value (1.07×10^{23}) was found for the synthetic polyisoprene.

It remains to account for the differences found between milled and unmilled natural rubber. These differences may not, of course, be representative. The proportion of microgel (Figure 2) may vary considerably from sample to sample[6], and one should not infer that heavy milling necessarily reduces the microgel content. It is reasonable, however, that the unmilled sample does not exhibit a low or zero value of A_2 since, as we have shown, this effect is due to the macrogel cyclohexane-insoluble fraction (Table IV).

CONCLUSIONS

Both synthetic and natural polyisoprenes contain a high scattering component(s) which can be partially removed by filtration. With milled natural rubber this causes $\bar{M}_w$ to increase and A_2 to diminish to zero as the solvent power of the solvent is increased. From this, from the constancy of Φ, and from the differences in $(\bar{r}^2/M)^{\frac{1}{2}}$ between natural and synthetic polyisoprenes it is considered probable that the component is a compact (and therefore presumably branched) species. The light-scattering behavior of synthetic polyisoprene is essentially normal, except for high values of $\bar{M}_w$ in chloroform. The possibility cannot yet be entirely excluded that some of these effects are due to nonrubber components. As with other polymers, notably polyethylene and polyacrylonitrile, microgel leads to considerable distortion of the Zimm diagram.

SYNOPSIS

The light-scattering behavior of solutions of natural and synthetic *cis*-1,4-polyisoprene is described. For milled natural rubber values of $\bar{M}_w$ increase as the solvent power of the solvent is increased and, at the same time, the second virial coefficient tends to zero. These effects may be due to compact (e.g., branched) structures. With unmilled natural rubber there is evidence for the existence of microgel. Synthetic polyisoprene shows the behavior expected of a linear polymer.

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A PROPOSED METHOD FOR ESTIMATING POLYMER MOLECULAR WEIGHT DISTRIBUTION WITHOUT FRACTIONATION *

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INTRODUCTION

The molecular weight distribution of a polymer is known to have important effects on rheological behavior and physical and mechanical properties. However, these relationships have not been extensively explored because accurate experimental determination of molecular weight distribution is, at best, difficult and time-consuming. F. Bueche and Harding[1] are the first to have achieved the goal of deducing the distribution of a (crosslinkable) polymer without experimental fractionation. Proceeding from the statistical relationship[2]

$$w_s = \sum_{y=1}^{\infty} w_y[1 - \rho(1 - w_s)]^y \tag{1}$$

between the weight fraction of sol w_s in a partially crosslinked system of crosslink density ρ, and the weight fractions w_y of primary y-mer molecules, they developed a method of calculating the w_y values from experimental values of w_s and ρ. This is an important advance because it circumvents the laborious task and the uncertainties of fractionation, but it is still not so simple as one might wish. The Bueche-Harding method requires considerable experimental data on sol-gel ratio versus crosslink density, a separate determination of an average molecular weight to serve as a kind of "normalizing factor," and some five hours of computations. It also requires either data on the kinetics of crosslinking or else the assumption that the kinetics are at least approximately of first order. Their success, nevertheless, has inspired the present attempt to develop a simpler method. This is proposed below and it is admittedly in a form very likely capable of refinement. Present data for testing its accuracy are quite limited, and until more experimental information becomes available one should regard it as an estimation method, its chief usefulness at present being restricted perhaps to comparative studies on a given polymer system.

DERIVATION OF DISTRIBUTION PARAMETERS

We assume that the molecular weight distribution conforms to Tung's empirical function. On inserting the latter into Equation (1) one can solve the resulting expression explicitly for the distribution parameters. The differential form of the function can be written:

$$w_y = abM_0^{b-1}y^{b-1} \exp\{-aM_0^b y^b\} \tag{2}$$

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where $y = M/M_0$ is the degree of polymerization, and a and b are important empirical parameters. Tung[3] has shown that Equation (2) fits quite well his fractionation data for several different polyethylenes, as well as published data for nylon 66, polymethyl methacrylate, and polystyrene. It also fits data for other polystyrene samples and for polyethylene terephthalate[4, 5]. With the possible exception of some (but not all) polyethylenes reported by Tung, Equation (2) is therefore applicable to a variety of chemically different polymers synthesized by different methods. The goodness of fit is not surprising, because the mathematical form of Equation (2) approximates some less empirical functions proposed by others. Green[4] has tested this point by comparing Equation (2) with the functions of Schulz[6], Wesslau[7], and Beasley[8]. He has shown, with data for five different polymers, that the Tung function gives results which are practically identical with those from the Schulz binomial distribution, but the results from the Wesslau and Beasley functions not only differ from those of Tung and Schulz, but also from each other. The simplicity and rather wide applicability of the Tung function, and its close agreement with that of Schulz, therefore make it a reasonable choice for the present treatment. As a further advantage, its two parameters are simply related[3,4] to the various average molecular weights and to the polydispersity by the equations:

$$\bar{M}_n = a^{-\beta}/\Gamma(1-\beta) \tag{3}$$

where $\beta = 1/b$

$$\bar{M}_w = a^{-\beta}\Gamma(1+\beta) \tag{4}$$

$$\bar{M}_v = a^{-\alpha\beta}\Gamma(1+\alpha\beta) \tag{5}$$

$$\bar{M}_w/\bar{M}_n = \Gamma(1+\beta)\Gamma(1-\beta) \tag{6}$$

In these equations Γ is the gamma function, and α in Equation (5) is the exponent in the viscosity equation $[\eta] = K\bar{M}_v^{\alpha}$. The maximum in the differential distribution curve is located by

$$M_{\max} = [(b-1)/ab]^{\beta} \tag{7}$$

On substituting Equation (2) into Equation (1) and letting $aM_0^b y^b = x$, we obtain

$$w_s = a^{1/b}\, bM_0^{b-(1/b)} \sum_{y=1}^{\infty} x^{1-(1/b)} [1-\rho(1-w_s)]^{(x/aM_0^b)^{1/b}} \exp\{-x\} \tag{8}$$

The second term within the brackets is much less than one, because $(1-w_s)$ is always less than one in a crosslinked system and the crosslink density even in a fairly highly crosslinked network is usually of the order of 10^{-2} or less. We can therefore expand the quantity in brackets and drop higher terms. Substituting this approximation in Equation (8) and changing the summation to an integral with zero lower limit, we obtain

$$w_s = a^{1/b}\, bM_0^{b-(1/b)} \left\{ \int_0^{\infty} x^{1-(1/b)}\, e^{-x}\, dx - [\rho(1-w_s)/(aM_0^b)^{1/b}] \int_0^{\infty} x e^{-x}\, dx \right\} \tag{9}$$

The first integral is finite if b is not less than 0.5. (This would apparently exclude one sample of polyethylene for which Tung reported $b = 0.386$; all other b values reported in the literature are larger than 0.5, and are mostly in the range of 1.5–2.5.) Integration of Equation (9) yields the final result

$$w_s = \frac{a^{1/b} b M_0^{b-(1/b)} \{\Gamma[2 - (1/b)] - [\rho/(aM_0^b)^{1/b}]\}}{1 - bM_0^{b-(1/b)-1}\rho} \tag{10}$$

This equation relates the weight fraction of sol to the crosslink density and to the molecular weight distribution parameters.

APPLICATION OF EQUATION (10)

Distribution data reported in the literature are usually for "original" polymers, whereas the present method, or that of Bueche and Harding, will reflect any changes which may have occurred in the milling or processing of a vulcanizable mixture. The distribution in the latter condition is frequently the more important; for example, it is the distribution that will govern vulcanizate properties. The "rheological distribution" governing processing will be some sort of time average of the original and final distributions, and will generally depend on a complexity of mechanical and chemical factors.

In order to determine a and b from Equation (10), one requires values of w_s and ρ for only two different states of crosslinking. One of these states should be low enough to yield an appreciable sol fraction (say, 5 or 10%) in order to minimize errors in the computed parameters. However, it should not be excessively low, for reasons to be explained later. If the two states of crosslinking are represented by subscripts 1 and 2, it is easily shown from Equation (10) that

$$bM_0^{b-(1/b)-1} = \frac{(w_{s1} - w_{s2})}{(\rho_2 - \rho_1) + (w_{s1}\rho_1 - w_{s2}\rho_2)} \tag{11}$$

The two sets of experimental values of w_s and ρ (suitably corrected as explained below) are substituted into Equation (11), along with the known molecular weight M_0 of the monomer unit, and the value of b is easily computed by trial and error. The value of a then follows from Equation (10), which can now be expressed in the more convenient form

$$a^{1/b} = \frac{w_s + bM_0^{b-(1/b)-1}\rho(1 - w_s)}{bM_0^{b-(1/b)}\Gamma[2 - (1/b)]} \tag{12}$$

The various average molecular weights, the poly-dispersity, and the maximum in the distribution curve are then simply computed from Equations (3) to (7). If one of the average molecular weights happens to be known from other measurements, comparison with the corresponding calculated value can, of course, be made to check the accuracy of the method for the particular system under consideration.

ESTIMATION OF "TRUE" CROSSLINK DENSITY

Corresponding values of w_s and ρ can be determined from a single swelling experiment, and the expected precision in w_s should ordinarily be within a few per cent. If the polymer system contains an appreciable amount of nonpoly-

meric contaminants such as soaps or other extractable ingredients, a correction will, of course, be required. Pertinent information is usually available from analytical data or from the conditions of polymerization or compounding. Some typical computations with Equations (11) and (12) show that the values of a and b are relatively insensitive to the normal precision in w_s, and b is relatively insensitive to that in ρ. However, since in actual computations the two terms in the numerator of Equation (12) are more or less equal in magnitude, a given error in ρ will lead to a comparable error in a, if b is of the order of 2. Therefore, even though ρ can be measured from swelling experiments within a precision of about 5% or less, provided that fairly good values of the polymer-solvent interaction constant are available, one still has to be concerned with its accuracy.

The value of ρ(physical) obtained from a swelling measurement depends in part on polymer statistical theory, and has been shown by Moore and Watson[9] to be, very roughly, about twice as large as the "true" value ρ(chemical) obtained from the chemical measurement of crosslinks in peroxide-cured natural rubber. The divergence depends on the crosslink density and, if the latter is not too small, we find from Moore and Watson's plots that

$$\rho(\text{chemical})/\rho(\text{physical}) = 0.811 - 17.1 \times 10^{-4}/\rho(\text{physical}) \qquad (13)$$

The value below which Equation (13) becomes invalid is about ρ(physical) $= 21 \times 10^{-4}$. Below this value, chain entanglements and free-end corrections become dominant, as Moore and Watson have shown, and the relationship between the crosslink densities becomes a function of molecular weight. Since comparisons between ρ(chemical) and ρ(physical) are not known for systems other than peroxide-cured natural rubber, we must assume for the time being that the correction factor given by Equation (13) is applicable to other polymers. Only future experiments will show how valid this is; but since the divergence is due to the physical factors mentioned, the assumption may be temporarily admissible. The values thus corrected should, in any event, be better than the uncorrected ones.

RESULTS FOR PEROXIDE-CURED SBR

In most published papers containing crosslink density values for vulcanized polymers there has been little reason, unfortunately, for reporting the corresponding sol fraction values. Information for testing the present method is therefore meager. Kraus[10] has published some data suitable for this purpose. Table 17 of his paper lists crosslink densities and "per cent extractables" for pure gum vulcanizates of cold SBR (Philprene 1500) which contained different concentrations of dicumyl peroxide and were cured for different lengths of time. The crosslink densities ν are reported in moles per cm^3. Assuming that his polymer contained butadiene and styrene units in the weight ratio of 75/25 and had a density of 0.93, one can convert the ν values to ρ values by dividing by 0.015. The latter, in turn, were corrected to ρ(chemical) by means of Equation (13). Kraus' values for "per cent extractable" also require correction for our purpose since, as he has pointed out[11], synthetic SBR emulsion polymers contain some 5–7% of fatty acid and soap; these contaminants will be included with the extracted sol. Inspection of his data shows that the "per cent extractable" values level out at a minimum value of about 6.9% in the pure gum systems, in good agreement with the quoted contaminant level. We have accordingly corrected the extractables values by this amount in order to obtain values of

TABLE I

DATA FOR PEROXIDE-CURED COLD SBR (BASED ON DATA BY KRAUS)

Dicumyl peroxide, phr	Cure time at 307° F, min	$\rho \times 10^5$, moles/cc (from swelling)	Extractables, %	$\rho \times 10^5$ (from ν)	$\rho \times 10^5$ (corrected)	w_s (corrected)
0.5	15	0.13	24.2	0.867	—	0.173
	30	0.19	18.3	1.27	—	0.114
1.0	15	0.47	13.1	3.13	0.83	0.062
	45	0.71	9.9	4.73	2.12	0.030
2.0	15	0.78	9.3	5.20	2.51	0.024
	30	1.32	6.9	8.80	5.42	0.0

w_s representative of the polymer sol fraction. As for M_0, we have employed a number-average value of 61, based on the assumed ratio of butadiene to styrene units in the polymer. Table I contains the data selected for these calculations, together with the corrected values. From the data given in the last two columns of Table I we have calculated the distribution values shown in Table II.

The distribution characteristics of the Philprene 1500 on which Table II is based are not known. However, Bueche and Harding[1] have reported values of $\bar{M}_n = 31{,}000$ and $\bar{M}_w/\bar{M}_n = 7$ for a compounded sample of cold SBR. Although their values are higher than those listed in Table II the agreement is not too bad when one considers that they arrive at their values by neglecting the lowest 10% of the polymer. Furthermore, their sample, which was prepared with sulfur, probably experienced less degradation during processing than did the peroxide-containing Philprene sample. Booth and Beason[12] have reported values of $\bar{M}_n = 80{,}000$ and $\bar{M}_w/\bar{M}_n = 3.4$ for a sample of type 1500 SBR that had not been subjected to any compounding or processing. In view of the differences mentioned, the results in Table II are therefore regarded as reasonable. The polydispersity values in Table II appear to increase with increasing peroxide content. This result, if significant, is concordant with the view that chain scission by the peroxide may have occurred. Statistical analyses have shown[13] that when random scission occurs, the original distribution broadens markedly during the initial stages, and not until an advanced state of scission has occurred does the polymer become more homogeneous as lower molecular weight species accumulate.

RESULTS FOR CROSSLINKED POLYSTYRENE

It is immaterial to the present method whether the polymer is crosslinked by a vulcanization reaction or by synthesis. If a trace amount of a suitable polyfunctional comonomer is used in the synthesis, the distribution characteristics of the product might be considered to approximate those of the "pure"

TABLE II

CALCULATED DISTRIBUTION VALUES FOR PEROXIDE-CURED COLD SBR

Dicumyl peroxide, phr	Tung parameters		Molecular weights $\times 10^{-4}$			Polydispersity
	a	b	$M_{max.}$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.5	—	—	—	—	—	—
1.0	1.63×10^{-9}	2.084	1.20	1.46	0.966	1.51
2.0	1.48×10^{-7}	1.782	1.56	0.605	0.338	1.79

homopolymer prepared under the same synthesis conditions. Or alternatively, the homopolymer distribution features might be deduced by extrapolation from products containing several small, but different, comonomer concentrations. Boyer and Spencer[14] have published extensive crosslinking and swelling data for slightly crosslinked polystyrene containing trace amounts of divinylbenzene as comonomer. We have computed ρ values from their values of M_c, but we were not able to correct these in accordance with Equation (13) because they were too small. We have estimated the corresponding values of w_s, from their data on short- and long-time equilibrium swelling ratios. Table III contains these data and the calculated distribution values. The average molecular weights appear to be reasonable, although they may be high by a factor of perhaps two, because of the use of uncorrected ρ values. The polydispersity, which can be shown to be practically independent of this correction, agrees rather well with the value of 1.41 (for $\bar{M}_w/\bar{M}_n$) which Booth and Beason have recently determined from Guzman's fractionation data[15] for a low-conversion polystyrene synthesized at room temperatures. It is interesting that the calculated value of b (2.358) agrees closely with that of 2.27 which Tung derived from Schulz and Dinglinger's fractionation data[16] for a "pure" polystyrene. While agreement

TABLE III

DISTRIBUTION VALUES FOR DIVINYL BENZENE CROSSLINKED POLYSTYRENE (BASED ON DATA BY BOYER AND SPENCER)

DVB, wt-%	$\rho \times 10^4$ (swelling)	w_s	Calculated distribution values
0.0333	4.59	0.120	$a = 2.28 \times 10^{-12}$
0.0462	7.89	0.059	$b = 2.358$
			$\bar{M}_w = 7.65 \times 10^4$
			$\bar{M}_n = 5.58 \times 10^4$
			$\bar{M}_w/\bar{M}_n = 1.4$

might be expected, since both values are based on the use of the same distribution function, the values nevertheless represent two rather different polymer samples. The agreement suggests that the presence of a trace of comonomer during synthesis influences a much more than b. However, since the Tung distribution is empirical, one can do little more than speculate about the possible fundamental significance of this observation.

CONCLUSION

The close agreement which Green has demonstrated between results from the Schulz binomial and the Tung distribution and the applicability of the latter to a variety of fractionation data for different polymers both seem to outweigh possible objection that the present method assumes a particular distribution function. Green's results suggest to us that the apparent exceptions found by Tung for some polyethylenes containing large amounts of low molecular species may possibly be attributed to fractionation inefficiency, rather than to the inadequacy of his function. The internal consistency or smoothness of data does not, of course, constitute proof of precise fractionation. In fact, one can safely say it is no easy matter to find complete fractionation data, of established precision, that can provide a critical test of a distribution function over the entire molecular weight domain.

In his study of polyethylenes, Tung suggested that his function tends to exaggerate the low molecular weight end of the distribution, in the sense that

the $\bar{M}_n$ values calculated from his parameters were only about half as large as those obtained by summation of the experimental data for the fractions. His calculated and experimental values of $\bar{M}_w$, on the other hand, were in satisfactory agreement. One might be tempted to use this to reconcile the $\bar{M}_n$ values of the SBR system in Table II with the higher values reported by others. However, this procedure would be indefensible because simply doubling the $\bar{M}_n$ values would give polydispersity values of less than unity. It would therefore seem incorrect to generalize that the Tung function gives abnormally small $\bar{M}_n$ values for all polymers, especially when there is some reason to believe that it is better than it seems, even for polyethylenes. Much more likely, the differences between the average molecular weights and the polydispersity of the peroxide-SBR system of Table II, and the corresponding quantities reported by Bueche and Harding for sulfur-SBR and by Booth and Beason for uncompounded SBR, are real and are due to chemical and other factors already mentioned.

Although the meager data at hand leave some question as to the accuracy with which the present method can predict absolute values of the various average molecular weights, the key to the matter seems to be the ratio of the true to the physically measured crosslink density for polymers in general, rather than the particular distribution function employed here. Less uncertainty is attached to the polydispersity, since this is a function of only one parameter, b, which is quite insensitive even to large errors in ρ. The method may therefore be useful, even in its present state, for comparative studies in a given system. These might include, for example, the effect of synthesis or processing variables on distribution characteristics and product properties or the effects of stabilizers in aging or other degradative processes.

SYNOPSIS

A method is proposed for estimating rather simply and with relatively little experimental data the molecular weight distribution characteristics of any crosslinkable polymer which follows the Tung distribution function. This function is combined with a fundamental relationship from the statistical theory of sol-gel ratios in randomly crosslinked polymers, to yield a result which relates explicitly the sol-gel ratio, the crosslink density, and the molecular weight distribution parameters. These parameters give the various average molecular weights and the polydispersity by simple computation. The method has been tested with meager data available for a peroxide-cured SBR and a divinyl benzene-crosslinked polystrene. Reasonably satisfactory results were obtained. A critical test of the absolute accuracy of the method requires experimental data not now available, and some refinements may eventually have to be made. However, the method should be useful, in its present state, for estimating distribution characteristics and, especially, for comparative studies within a given polymer system.

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NOTE CONCERNING EQUATIONS (9) THROUGH (12)

Equations (9) through (12) contain a mathematical error which on correction yields

$$w_s = \{a^{1/b}bM_0\Gamma[2 - (1/b)] - b\rho\}/(M_0 - b\rho) \tag{10'}$$

$$b = M_0(w_{s1} - w_{s2})/[\rho_2(1 - w_{s2}) - \rho_1(1 - w_{s1})] \tag{11'}$$

and

$$a^{1/b} = [w_sM_0 + b\rho(1 - w_s)]/bM_0\Gamma[2 - (1/b)] \tag{12'}$$

However, application of these corrected equations to the data of Tables I and III gives b values some 10^3 as large as the literature values cited.

In order to determine whether the Tung function might in some way be responsible for these unacceptable results, we have repeated the derivation, using the Schulz distribution

$$w_y = [z^{k+1}/\Gamma(k + 1)]y^k \exp(-zy) \tag{2'}$$

instead of Equation (2). Here, the parameters are related to the number- and weight-average degree of polymerization by

$$z = k/\bar{P}_n = (k + 1)/\bar{P}_w \tag{2''}$$

When Equation (2') is inserted in Equation (1), along with the approximation $[1 - \rho(1 - w_s)]^y \cong \exp[-y\rho(1 - w_s)]$, and the summation is changed to an integral with zero lower limit, we obtain

$$(w_s)^{1/(k+1)} = z/[z + \rho(1 - w_s)] \tag{14}$$

Simultaneous solution of the equations obtained by substituting two sets of experimental values of ρ and w_s into Equation (14) yields z for any chosen value of k. Substitution of z and w_s (exp.) into the right member of eq. (14) yields a calculated value of the left member. By plotting $[w_s(\text{calc.})/w_s(\text{exp.})]^{1/(k+1)}$ against k, one can obtain the k value at which $w_s(\text{calc.}) = w_s(\text{exp.})$. Application of this method to the crosslinked polystyrene data of Table III yields $k = 0.42$ and $z = 1.18 \times 10^{-4}$. The $\bar{M}_n$ value obtained by substituting these parameters into Equation (2'') is 370,000; this agrees fairly well with the value of 300,000 reported by Boyer and Spencer for their polystyrene made without addition of divinyl-benzene to the polymerizing system. The polydispersity ($\bar{P}_w/\bar{P}_n$) according to Equation (2'') is 3.4. Boyer and Spencer did not report a value for this quantity, but our value is higher than that (1.4) reported by Booth and Beason for a different sample of polystyrene. Application of the present method to the SBR data of Table I failed to yield any positive value of k which satisfied the data. We are unable to explain this result at present.

We are indebted to Dr. A. M. Kotliar for bringing the above error to our attention, and for several valuable suggestions.

THE NATURE OF STATIC FRICTION IN ELASTOMERS

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In contrast with kinetic friction, the static friction of rubber has had insufficient attention paid to it. This is explained by the fact that the investigation of so-called static friction meets with experimental difficulties as a result of the peculiar frictional properties of rubberlike polymers[1–4].

As a result of this a number of authors[5–7] have avoided the direct measurement of the static friction of rubber, replacing it by the measurement of friction at a constant low rate of slip, assuming that this value is close to the static friction. But in some work[8,9] there has been observed a tendency to the disappearance of friction of rubber on steel with reduction in the rate of slip to zero, while in work by one of the present authors[10] a conclusion is drawn as to the existence with rubber of friction of the same nature as with hard bodies.

Tests which we instituted with a pendulum tribometer led to the conclusion that the accuracy of this method is inadequate for the reliable determination of the static friction of elastomeric materials. In Figure 1 we show a curve plotted with the tribometer for the system rubber-steel (curve *1*). The instant of the departure of the curve from the axis of the ordinates, according to Reference 10, corresponds to static friction. The accuracy with which the departure of the curve from the axis of the ordinates is recorded is equal to the thickness of the record on the drum for the curve, 0.2 to 0.3 mm.

This "admissible" 0.2 to 0.3 mm corresponds to the movement of the testpiece up to the moment of visible departure of the curve from the vertical axis. In an analogous method, by Roth, Driscoll and Holt, this distance was taken as 0.5 mm[5].

We obtained curve 2 in experiments with a viscous fluid held in a steel jar, in which a piston is allowed to move freely. As may be seen, the flow diagram of the viscous fluid does not differ qualitatively from that of rubber friction, as a result of which a similar method could not be adopted for the determination of static friction.

In[5,10] there is determined the friction occurring at the moment when the rubber testpiece moves by a certain small amount (the "admissible") determined by the accuracy of the reading. From now on the force of friction determined in this way will be designated as the "initial force of friction".

While "steady" (or "dynamic") kinetic friction depends upon the rate of slip, the load and the temperature, the initial friction of rubber is a more complicated value, since it depends also upon the time of prior contact. This dependence is clearly evident if the time varies within the range of a few minutes; with longer times of prior contact the initial friction remains practically constant. In order to exclude the influence of this factor, the time of prior contact was fixed at 3 min in all experiments.

* Translated from Vysokomolekularnye Soedineniya 2, No. 2, 238–42 (1960) by R. J. Moseley; a translation of the Rubber and Plastics Research Association of Great Britain.

The measurements were carried out on the NIIRP (Rubber Research Institute) tribometer[11], in which it is possible to apply various constant rates of movement and to affix interchangeable dynamometers of various degrees of stiffness. The dynamometers are inserted between the rubber and the tractive device. Since in the experiments we are applying a rate of movement at the output of the tractive device, some time is necessary for the dynamometer to

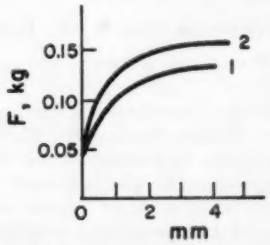

FIG. 1.—Curves plotted with the pendulum tribometer for the forces of external and internal friction as a function of the extent of travel of the tractive device with increasing tractive force (rate of traction 50 mm/min): *1*—External friction of SKN-18 rubber on steel with small load; *2*—Internal friction of a high-viscosity fluid (a solution of rubber).

come into operation; the stiffer the dynamometer, the shorter this time and the more rapidly is the tractive force applied to the testpiece.

In Figure 2 we show the results of measurement of the initial force of friction with an allowance of 0.15 mm, obtained on dynamometers of various stiffness at a rate of traction of 0.08 mm/sec. By the stiffness we understand the magnitude of the force necessary for the deformation of the force device of the dynamometer by 1 mm. The stiffness of the pendulum dynamometer on which

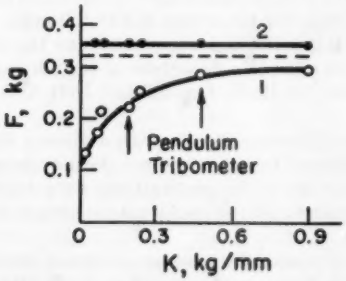

FIG. 2.—Relationship between the tangential force (the reading on the dynamometer) and the stiffness *K* of the dynamometer in the friction on SKN-26 rubber on steel. Rate of the tractive device 0.08 mm/sec: *1*—initial friction; *2*—steady friction.

in Reference 10 there were carried out the measurements to demonstrate the existence of static friction in rubber depends upon the size of the load and upon the angle of deflection of the pendulum; the region of stiffness of this dynamometer is marked off in the figure by the arrows.

With increasing stiffness of the dynamometer the initial force of friction tends towards the value found on a dynamometer of great stiffness. These experiments provide evidence that the measured initial force of friction depends upon the rate of application of the tangential force and that the data of

the various authors can be compared only with the proviso that sufficiently stiff dynamometers are being used, which in practice means dynamometers on the tensometric principle. The stiffness of such a dynamometer in our measurements was of the order of 10^3 kg/mm. The broken line in Figure 2 indicates the friction measured with this dynamometer.

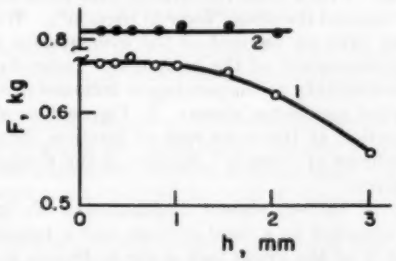

FIG. 3.—Relationship between the reading of the dynamometer and the height of the working portion of the testpiece in friction of SKN-26 rubber on steel. Rate of traction 50 mm/sec; *1*—initial friction; *2*—steady friction.

On increasing the stiffness of the dynamometer, which corresponds to a reduction in the time of application of force, the initial force of friction increases. The force of friction with a sufficiently stiff dynamometer lies close to "steady" kinetic friction, which does not depend upon the stiffness of the dynamometer and is therefore conventional.

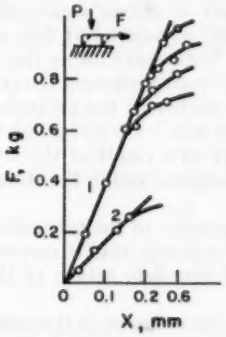

FIG. 4.—Relationship between tangential force and the extent of movement in friction of a natural rubber vulcanizate on steel: *1*—with normal loading, 1.4 kg/sq cm and rates of traction v_1—0.8, v_2—$8 \cdot 10^{-2}$, v_3—$8 \cdot 10^{-3}$, v_4—$8 \cdot 10^{-4}$ mm/sec; *2*—with normal loading, 0.8 kg/sq cm and rate of traction $8 \cdot 10^{-4}$ mm/sec.

With the application of a tangential force we observed in addition to the slip an elastic shear of the testpiece. The extent of the elastic shear is proportional to the applied force, while the rate of slip depends nonlinearly upon the tangential force and with small forces becomes vanishingly small. As a result, as Hurry and Prock have observed[8], the investigation of friction with small forces becomes difficult.

From this it follows that with small admissible movement the elastic shear, which takes place rapidly, may completely mask the slip of the rubber; the

stiffer the rubber and the less the working thickness of the testpiece, the smaller the contribution of the elastic movement to the whole.

In Figure 3 we present the relationship between the internal force of friction measured with the pendulum tribometer and the thickness of the working portion of the testpiece with an admissible movement X of 0.5 mm and rate of traction 50 mm/min. Under these conditions, with thicknesses up to 1 mm, we observe practically one and the same "force of friction". With large thicknesses the measured value falls on account of the ever greater contribution of the elastic shear to the movement of the testpiece. These data lead to the conclusion as to the unsuitability of the pendulum tribometer for the measurement of friction in the initial moment of shear. In Figure 3 we also present data for "steady" kinetic friction at the same rate of traction, from which data there follows the independence of "steady" friction of the thickness of the working portion of the testpiece.

If the testpiece of rubber, shown diagrammatically in the top corner of Figure 4, is firmly attached to a hard surface, and a tangential force applied, then the movement X of the upper face of the testpiece, to which this force F, takes place only through shear deformation. Loading and unloading in succession showed that a natural rubber vulcanizate regained its shape completely after unloading (i.e., the movement was zero). These results made it possible to apply the method of unloading as a method of dividing the total movement into reversible and irreversible components, a fact which has not received attention in previous work. The irreversible component of movement relates to the slip of the rubber on a hard surface. The exclusion of elastic movement is particularly important in the testing of soft vulcanized rubbers, for which the shear modulus is relatively small.

In Figure 4 the upper set of curves shows the relationship between the tangential force and the total movement at four rates of the traction device (with stiff dynamometer). With small forces the data fall on a straight line, which is evidence of proportionality between the stress and the deformation of elastic shear; the stiffer the rubber or the greater the normal load, the nearer this line comes to the vertical axis. On increasing the normal load the slope of the line increases, apparently as a result of the alteration in the thickness of the working portion of the testpiece and in the stiffness of the material which is in a complex stressed states.

The greater the rate of increase of the tangential force, in a wider range of change of force do we observe purely elastic movement. Unloading used as a reference invariably showed complete return of the testpiece to the original position.

Attention is attracted by the influence of the rate of application of tangential energy upon the instant of departure of the data from the straight line. The instant of departure from the straight line corresponds to a movement of the testpiece relative to the backing by an "admissible" 0.05 mm and to a force of friction which we may call the conventional static friction.

The data in Figures 2 and 4 agree, since in either case the initial force of friction is all the greater the higher the rate of application of the force.

The data presented show clearly that the initial friction is kinetic in nature, as a result of which we also observe its dependence upon the rate of increase in the tangential force. Therefore the measured value must not be identified with static friction, by which we understand the existence at the contact of two surfaces of a force limit, below which slip is not observed however long we wait.

From the molecular-kinetic theory of friction of rubber[3] it follows that there

is no static friction with rubber in the strict sense of the word. However in practice the initial friction may be utilized as an engineering characteristic with due regard to its dependence upon time factors (the time of motionless contact, the rate of application of the force and so on). For this practical purpose the initial friction may be designated as conventional static friction.

CONCLUSIONS

1. A method free from the shortcomings of earlier work is proposed for the measurement of the friction of elastomeric materials in the initial moment of shear.

2. From results of measurement of friction of rubber on steel it follows that static friction, determined as the coefficient of friction in the initial moment of slip, is a conventional parameter, since it depends upon the accuracy of measurement of the movement and upon the rate of application of the tangential force.

3. The conventional coefficient of static friction of elastomeric materials is particularly evident at low rates of application of the tangential force, which fact is connected with the nature of dry friction of rubberlike polymers.

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MECHANICAL DEGRADATION OF HIGH POLYMERS *

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INTRODUCTION

Mastication of rubbers and molten plastics often gives rise to degradation of the polymer molecules[1, 2]. The amount of degradation is severely dependent upon shear rate, melt viscosity, and molecular weight of the polymer, temperature, and the presence of plasticizer. Under certain conditions, usually at low temperatures, one finds that the presence of oxygen is only of minor importance. At high temperatures, at least in certain cases, shear degradation is seriously increased when oxygen is present, even though very little degradation occurs without mastication. In this latter case, oxidative scission does not appear to take place at random along the chain but seems to occur predominantly in the central portion of the chain[1a].

The purpose of this paper is to present a molecular theory which unifies these various observations. It will be restricted to the mechanical actions involved during mastication. The effect of oxygen on mechanical degradation will also be considered.

MOLECULAR PICTURE

Consider the polymer molecule shown in Figure 1. If this molecule is immersed in a viscous matrix, polymeric or otherwise, and the matrix is subjected to a shearing action as illustrated, the viscous matrix will cause the molecule to rotate in a clockwise direction.

It can be shown[3] that the molecule will rotate with a frequency $(\frac{1}{2})\dot{\gamma}$, where $\dot{\gamma}$ is the shear rate. The combined effect of this rotation and the flow of the pervading matrix[3] is to stretch the molecule along the line OO′ and compress it along the line II′. Of course, since the molecule is rotating, a given segment will first be pulled out towards O, then pushed in from I′, pulled out towards O′, and so on. In fact it can be shown that each segment oscillates back and forth in a sinusoidal type motion.

It is tempting to speculate that at very high shear rates the chain will be stretched enough along OO′ so as to cause it to break. The current theories of molecular viscoelasticity enable one to compute how much the molecule is distorted by the shearing forces, and this is done in Appendix I. It turns out that the molecule is not stretched enough by this action to give rise to any sizeable amount of degradation. The reason for this is quite simple. At very high shear rates, the molecule rotates so fast that the chain does not have time to stretch very much. For example, a segment rotating past O will be pulled away from the center of the molecule, but before it moves out very far it has already rotated to I′, where it is being pushed back in. The net result is that

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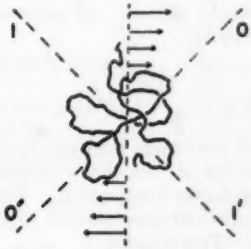

FIG. 1.—A typical polymer molecule in a sheared liquid.

the molecular distortion increases as the shear rate increases, but at very high shear rates the molecule approaches a certain limiting amount of distortion which is far too small to cause the chain to break.

The speculations of the preceding paragraphs are valid provided the matrix in which the polymer molecule is imbedded consists of small molecules. On the other hand, if a polymer molecule is immersed in a matrix of other polymer molecules, another complication must be considered, the entanglement of the molecules. It turns out, as shown in the following, that these entanglements give rise to very large tensions near the central portions of the molecules.

When a molecule entangled with other molecules is sheared, it is necessary that the molecules disentangle from each other in order for flow to occur. Even though the shear rate may be small and the molecule is not greatly distorted, the segments of the molecule must move very swiftly if the entanglements with surrounding molecules are to be released without the development of very large forces. This movement within a molecule, which is necessary if the entangled chains are to be released, is known to be of major importance in determining the viscosity of such systems[4]. Its importance for shear degradation may be shown by reference to Figure 2.

COMPUTATION

Figure 2 is a schematic diagram showing the action of entanglements when a molecule is subjected to a tensile shear $\dot{\gamma}$ in the x direction. Suppose the molecule consists of Z links, each link having a molecular weight M_0. Denote the molecular weight between entanglements by M_e. On the average, two entanglement points such as A and B will separate with a velocity $(\frac{1}{2})\dot{\gamma}a_0$ under the action of the shearing forces.

If segment AB is taken to be the central one, it will not move even though it is elongating. However, each link in the two adjacent segments, AY and

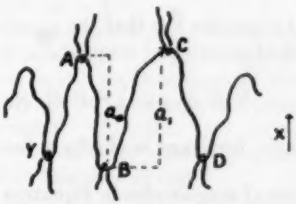

FIG. 2.—A schematic diagram showing the action of entanglements.

BC, must move with a velocity $(\frac{1}{2})\dot{\gamma}a_0$. In general, each link in the ith segment must move with a velocity

$$(\tfrac{1}{2})\dot{\gamma}\sum_{n=0}^{i-1} a_n \tag{1}$$

The velocities indicated are made possible by appropriate tensions along the molecule. A link moving at velocity v resists movement by a viscous force, fv, where f is a friction factor for the link. The tension on the center link of the chain is the sum of all the forces needed to pull either side of the chain through its entanglements. This tension is

$$F_0 = \sum_{i=1}^{M/2M_e} \left[(M_e/M_0)(\tfrac{1}{2})(\dot{\gamma}f) \sum_{n=0}^{i-1} a_n \right]$$

or (see Appendix II)

$$F_0 = (\tfrac{1}{16})\dot{\gamma}f(M_e/M_0)^{\frac{1}{2}}(M/M_e)^2 l \tag{2}$$

where a, the mean x-directed end-to-end distance of a chain of molecular weight M_e, is taken to be $l(M_e/M_0)^{\frac{1}{2}}$, with l the length of a chain link.

The tension in the qth link from the center is obtained in the same way (see Appendix II) and is

$$F_q = F_0[1 - (4q^2/Z^2)] \tag{3}$$

The chance that a chain bond subjected to a tension F will break in time dt is given by[5]

$$\omega \exp\{-(E - F\delta)/kT\}dt \tag{4}$$

In this expression E is the energy needed to break the bond, ω is the bond vibration frequency and δ is a distance approximately equal to the distance the bond will stretch before breaking.

The chance that the chain will break in time dt is the sum of the changes for the individual bonds

$$Pdt = dt \sum_{q=0}^{Z(\frac{1}{2})} \omega \exp\{-(E - F_q\delta)/kT\} = (Z/4)(\pi kT/F_0\delta)^{\frac{1}{2}}\omega \times \exp\{-(E - F_0\delta)/kT\}E_2[(F_0\delta/kT)^{\frac{1}{2}}]dt \tag{5}$$

where $E_2[x] = \int_0^x \exp\{-y^2\}\,dy$

If P is independent of time, one has that the number of chains N remaining unbroken after time t out of an original number N_0 is[5]

$$N = N_0 \exp\{-P\omega t\} \tag{6}$$

Therefore, the rate of chain breakage is chiefly a function of P since ω is essentially constant.

By examining the order of magnitudes in Equation (6) one can show that if the chain is to break in any reasonable time, then $F_0\delta/kT > 2$ and so one has

to good approximation

$$P = \omega(Z/4)(\pi kT/F_0\delta)^{\frac{1}{2}} \exp\{-(E - F_0\delta)/kT\} \tag{7}$$

In addition, E/kT will be of the order of 10^2, and so the exponential factor will vary much more rapidly with the temperature and molecular variables than do the factors in front of it. We therefore write

$$P = K \exp\{-(E - F_0\delta)/kT\} \tag{8}$$

where K is essentially a constant.

It remains yet to express the friction factor f in terms of molecular weight and viscosity. This is easily done if all the molecules are of the same length. In that case, one has for high molecular weights[4]

$$f = (288/\rho N)(M/R^2)(M_e/M)(M_0/M)\eta \tag{9}$$

where ρ is the polymer density, R is the root-mean-square chain-end distance, N is Avogadro's number, and η is the shear viscosity at negligible rate of shear. Even if the polymer is heterogeneous, f is still given by the above relation, provided M is replaced by M_t, an average molecular weight intermediate between the weight- and Z-average[6]. One therefore has, in place of Equation (2),

$$F_0 = (\eta\dot{\gamma})(18/\rho N)(M_t/R_t^2)(M_e/M_0)^{\frac{1}{2}}(M/M_t)^2 l \tag{10}$$

The molecular weight without subscript in Equation (10) refers to the molecule which supports the force F_0 at its center.

DISCUSSION

A. LOCATION OF THE BREAK

From Equation (3) one sees that the force along the chain reaches a maximum at the center. Therefore the most probable place for the chain to break is at its center. This fact was first discovered by Fren'kel[7] many years ago. In general, the ratio of the number of chains which break at the qth link from the center to the number which break at the center is, from Equation (4)

$$\exp\{-(F_0\delta/kT)(4q^2/Z^2)\} \tag{11}$$

Since $(F_0\delta/kT)$ will usually be of the order of 10 or 20, it is clear that the break will usually occur rather near to the chain center. For example, if $F_0\delta/kT = 20$, ten chains will break at the center for each chain which breaks $\frac{1}{3}$ of the way out from the center, i.e., where $2q/Z = \frac{1}{3}$.

An interesting case to consider is the degradation of a perfectly sharp polymer fraction. Suppose the shear rate is large enough to degrade the molecular weight being considered but is still small enough so that a chain half as long does not degrade appreciably. It will be seen in a later section that this condition is not difficult to achieve. Equation (11) may be used to predict the distribution of molecular weights after all the original molecules have been broken. It turns out that in this special case

$$M_w/M_n \cong 1 + (\tfrac{1}{2})kT/F_0\delta \tag{12}$$

If $F_0\delta/kT = 10$, then $M_w/M_n = 1.05$ and so the fraction will still be extremely sharp.

B. RATE OF DEGRADATION

The rate of chain breakage may be obtained from Equation (8) and is

$$Pdt = K \exp\{-(E - F_0\delta)/kT\}dt$$

If one restricts the discussion to a single type of molecule at a fixed density and temperature then F_0 can be written as

$$F_0 = (\text{const})\dot{\gamma}M^2M_t^{1.5} \tag{13}$$

In writing this, use has been made of the fact that $\eta = (\text{const})M_t^{3.5}$. Since M_t will vary with time as the molecules degrade, F_0 is not usually a simple function of time.

Consider first the special case where a few very high molecular weight molecules are present in a sample of much lower molecular weight. In this case the breakdown of the large molecules will not change M_t to any great extent and it can be taken as constant. Therefore, the rate of breakage of the large molecules of molecular weight M is given by Equation (6). Their number decays exponentially with a decay time τ which is given by

$$1/\tau = P\omega \tag{14}$$

Notice that since $P \sim \exp\{-F_0\delta/kT\}$ and since $F_0 \sim M^2$, the decay time τ is an extremely rapidly varying function of M. For example, if $F_0\delta/kT = 20$ for a given molecular weight M_0 which has a decay time τ_0, the decay time τ for a molecular weight $M = M_0/1.2$ is given by $\tau/T_0 = e^4 = 55$.

In the more general case where M_t must also be considered a function of time, the situation is much more complicated. For any given distribution one could, in principle, carry through a computation of the decay as a function of time. However, the main features of the decay process can be ascertained without doing this in detail. The initial part of the decay can be obtained from Equations (6), (10), and (14) from data for the original polymers. The final part of the decay can be inferred in a similar fashion from the final condition of the polymer.

C. MOLECULAR WEIGHT DISTRIBUTION

An examination of Equations (13) and (14) shows that the rate of degradation for a particular size molecule is severely dependent upon the molecular weight of the molecule. As seen in the previous paragraphs, it is not at all unreasonable to expect that a 20% change in molecular weight would cause the rate of degradation to change by a factor of 10^2. For this reason, it is to be expected that, after a material has been masticated for a while, essentially all the molecular weights above a certain critical value M_c will no longer be present. The original molecules with M less than M_c will be augmented by the decay products of the large molecules. It should be noticed that this is true only if one starts with a low shear rate and gradually increases it to its final value.

Given the initial distribution of molecular weights and with the assumption that M_c is sharply defined, the distribution after degradation is most easily

found by the following approximate procedure. All the original polymer having molecular weight $M_1 > M_c$ will appear in the final distribution as molecular weight $M_1/2^n$ where n is the smallest integer which will make $M_1/2^n < M_c$. This procedure assumes that the molecules always split exactly in the center and that τ varies extremely fast with M. Both of these assumptions are probably reasonably good.

If the original molecular weight distribution is a wide one, it is clear that mastication will narrow the distribution. As shown above, however, sharp distributions may actually be widened by mastication.

D. EFFECTS OF TEMPERATURE, DILUENT, AND SHEAR RATE

These three variables cause similar effects and are conveniently discussed together. One sees from Equation (10) that the above factors influence F_0 through the product $(\eta\dot{\gamma}/\rho)M_e^{\frac{1}{2}}$. Anything which increases the melt viscosity will increase F_0. If plasticizer is added, η will fall very markedly. In addition, M_e will increase with added plasticizer. This means, if one is to obtain comparable degradation in the presence of plasticizer, $\dot{\gamma}$ must be increased to compensate for the decrease in $\eta M_e^{\frac{1}{2}}/\rho$.

Increase in temperature will result in a large decrease in η and minor changes in ρ and M_e. Consequently, an increase in temperature must be compensated by an increase in $\dot{\gamma}$ if comparable degradation is to occur. Since activation energies for flow in these systems are usually of the order of 15 kcal/mole, the viscosity will change by a factor of about two for a 10° C temperature change. Therefore one would have to double the shear rate to compensate for a 10° rise in temperature. It is obvious that temperatures must be accurately maintained if reproducible mastication results are to be obtained.

E. DEGRADATION IN THE PRESENCE OF OXYGEN

If one considers the action of oxygen only in so far as it aids bond scission and ignores its effects upon other reactions, the effect of oxygen is nearly equivalent to reducing the energy E needed for bond rupture. Suppose that the temperature is low enough so that oxidative scission is slow in the absence of mastication. It may be that the temperature is high enough so that η, and therefore F_0, has decreased so much that chain breakage is negligible when mastication occurs in the absence of oxygen. However, if the material is masticated in the presence of oxygen, degradation may occur, since the oxygen has lowered E in Equation (8) and P may have become sizeable as a result. Since the shearing force and oxygen both act together to break a given bond, those near the center of the molecule will break most often.

Ordinarily one thinks of oxidative scission as being random. The present considerations show that oxidative scission, in a polymer which is being masticated, will occur at the most highly strained bonds. Consequently, if the temperature is not extremely high, the resultant molecular weight distributions will be those characteristic of shear degradation rather than random scission. At very high temperatures, the oxygen reaction will take place even without shear, and the distribution will change to that characteristic of random scission.

F. RELATION TO EXPERIMENTAL RESULTS

The theoretical results found here are in accord with the limited experimental data available[1,2]. Watson and co-workers have obtained experimental results

which confirm all of our results, at least in a qualitative way. Whether or not the agreement is quantitative is still unknown. Accurate measurement of degradation as a function of melt viscosity and molecular weight are needed before crucial tests can be made. It would also be of value to test the results concerning degradation of sharp fractions.

The present theory is incomplete. It ignores the complicating features of possible chemical reactions after the chains break. These effects can be minimized by the addition of inhibitors to the polymer. However, the general case, when subsequent reactions occur, is an interesting but complex subject untouched by the present theory.

G. RECENT RESULTS

Since the time that the body of this paper was submitted, a significant paper by Bestul[9] has appeared. Although his approach is far different from that of this work, he also concludes that intermolecular interactions are of paramount importance for mechanical degradation. He does not, however, arrive at a quantitative molecular theory for their effects in terms of entanglements.

APPENDIX I

The viscoelastic behavior of a polymer molecule immersed in a viscous medium and subjected to shear can be worked out by use of method previously outlined[8]. Knowing that the force on any link of the polymer molecule at a distance r from the mass center is given by $(\frac{1}{2})\dot{\gamma}r \sin(\dot{\gamma}t)$, one can substitute in the general equations previously formulated[8]. A first approximation for the motion of the links can be obtained by setting r equal to its average equilibrium value. The resultant oscillatory value found for r can then be subtracted from the assumed value to obtain a perturbation to the original average force. Assuming the system to be linear, this perturbation is used to obtain a second approximation. This process is repeated to give a convergent series for the displacement of any segment.

It is found that the amplitude of stretching of the center link of the chain is given to good approximation by

$$\Delta s = (4l/\pi Z^{\frac{1}{2}})\Phi[1 - (4\Phi/\pi^2)]^{-1} \tag{15}$$

with

$$\Phi = \dot{\gamma}\tau_1(1 - j\dot{\gamma}\tau_1)(1 + \dot{\gamma}^2\tau_1^2)^{-1}$$

where $j = \sqrt{-1}$. In this expression τ_1 is a characteristic relaxation time for the chain[8], Z is the number of links in the chain and l is the length of a link. The maximum value of Δs is about $l/Z^{\frac{1}{2}}$. The maximum tension in this link is[7] about $(l/Z^{\frac{1}{2}})$ $(3kT/l^2)$ and is much too small to cause the link to break in any reasonable time. In the same way, one can show that the chain end-to-end length is stretched far short of its maximum possible extension.

APPENDIX II

Equation (2) in the text is obtained by evaluating the following double sum:

$$S = \sum_{i=1}^{M/2Mo} \sum_{n=0}^{i-1} a_n \tag{16}$$

Since a_n is given its average value in each case, $a_n = a = l(M_c/M_0)^{\frac{1}{2}}$, it is a constant and one has

$$S = a \sum_{i=1}^{M/2M_e} i = (a/2)(M/2M_e)[(M/2M_e) + 1] \cong (a/2)(M/2M_e)^2 \quad (17)$$

This, when substituted in the expression given in the text, yields Equation (2).

Equation (3) is obtained in the same way, except now the limits on the outer sum must be changed. One has

$$S = \sum_{i=q}^{M/2M_e} \sum_{n=0}^{i-1} a_n \cong [(M/2M_e)^2 - q^2](a/2) \quad (18)$$

The use of this expression for the sums gives Equation (3) directly.

SYNOPSIS

A theory for the shear degradation of high polymers is presented. It assumes the molecules to exist in the rubbery or liquid state and does not include the effects of chemical reactions which might occur subsequent to chain rupture. The computation shows that the entanglements along the chains play a major part in the rupture process. Expressions for the rate of chain rupture are obtained in terms of the melt viscosity, shear rate, and molecular weight. Other factors enter also, but the sensitive variables are those listed. The variation of molecular weight distribution with shear degradation is considered. It is pointed out why oxidative scission during shear is not a random process. In general, the theoretical result agrees with the limited experimental data available.

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THE MECHANOCHEMICAL BREAKDOWN OF POLYSTYRENE BY VIBROMILLING *

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INTRODUCTION

Intensive mechanical treatment of natural and synthetic high polymers leads to molecular rupture and thus to breakdown of the macromolecules. A large number of papers on this have appeared, particularly in recent years, and only a few need be mentioned here. The mechanical breakdown of polymer chains can be brought about by mastication and milling[1,2,3], by rapid stirring of polymer solutions[4,5,6], by repeated flowing of polymer solutions through capillaries and nozzles under pressure[7,8], by ultrasonics[4,9,10,11] and in particular by *vibromilling*[12,13,14,15,16]. This paper deals with the use of this last method.

Staudinger and Heuer[7] were the first, in 1934, to settle the question of whether in the mastication of raw rubber there is a mechanical rupture of the chain molecules as well as the oxidative breakdown, by grinding tests on polystyrene as a model substance. These authors found a marked decrease in viscosity in tetralin solutions of polystyrene masticated under nitrogen and concluded from this that a mechanical rupture of the chain molecules is possible. In connection with this they considered it probable that also in the mastication of raw rubber a mechanical breakdown of the rubber molecules can take place, along with the oxidative. This assumption has since been confirmed by the work of Pike, Watson, Angier and others[1].

In the 1940s Hess and coworkers[12] carried out extensive investigations into the breakdown of high-polymeric materials (cellulose, polystyrene, etc.) in vibromilling. Hess was also the first, on the basis of these investigations, to designate the breakdown of macromolecular materials occurring in vibromilling as a "mechanochemical effect".

Nowadays all mechanical breakdown processes (milling, masticating, rapid stirring, etc.) are grouped together under a new branch of science *mechanochemistry of high polymers.*

Mechanochemistry is concerned with the interaction between mechanical and chemical energy. It is therefore the science of the chemical effects of mechanical energy and of the mechanical effects of chemical processes[17]. In the case of the breakdown of high polymers we investigate the scission by mechanical action and subsequent formation of chemical bonds.

The splitting of a macromolecule in the mechanical comminution of high-molecular materials is probably made possible by a localization of the mechanical energy at individual points on the polymer chain, which leads under certain conditions to internal stresses which exceed the strength of a covalent or electrovalent bond.

* Translated by R. J. Moseley from *Plaste u. Kautschuk* 6, No. 8, 361–4 (1959); translation 836 of the Rubber and Plastics Research Association of Great Britain. This article is an expanded version of a paper delivered to the Chemiedozententagung of the Chemische Gesellschaft in der DDR, Freiberg/Sa., June 1958.

The rate, degree and limit of the mechanochemical breakdown depend upon the chemical nature and the physical condition of the polymer as well as on the medium in which the breakdown is carried out (gaseous atmosphere, solvent, etc.) and the conditions of breakdown (in the case of vibromilling, e.g., the charge ratio, the amplitude, the size of the balls and specific gravity of the material of the balls, etc.). According to Baramboïm[13] the mechanical rupture of the macromolecules proceeds all the more intensively and rapidly the greater the rigidity of the polymer chains and the packing density of the macromolecules and the more capable the medium is of deactivating the active end groups of the breakdown products. Raising the temperature, increasing the flexibility and increasing the mobility of the chains all hamper breakdown in grinding and mastication of polymers[1]. Bearing in mind these findings and experiences it is possible to carry out in the shortest way and under definite conditions a controlled breakdown of a polymer to get a desired mean degree of polymerization or K value.

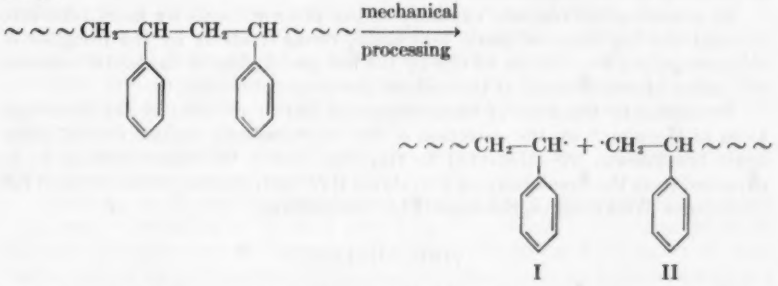
In the work by Staudinger and Hess nothing had hitherto been said about the chemistry of the mechanical breakdown reactions. It was merely established that in this mechanical rupturing of the chain molecules we are concerned not with a thermal breakdown but a chemical reaction, based primarily on a splitting of the macromolecules by mechanical energy. This has recently been confirmed by Baramboïm[21] and by our investigations.

The question of the mechanism of breakdown has been cleared up in essentials by the work of Pike, Watson[1], Kargin[20], Baramboïm[13] and Berlin[2,19] and the last few years.

Bearing in mind the fact that the macromolecues of polymers may contain both covalent and electrovalent bonds in the base chain, there are according to Berlin[18] three possible main mechanisms of rupture of the molecules under the action of mechanical forces: (a) radical mechanism, (b) ion mechanism and (c) radical-ion mechanism.

In the case of polystyrene there are only covalent bonds in the chain, so that in breakdown we may assume a radical mechanism with formation of macroradicals.

Then the scission of a C—C bond of a macromolecule leads inevitably to the formation of two types of macroradicals differing in the degree of delocalization of the untwinned electron and thus having also a different reaction capacity:

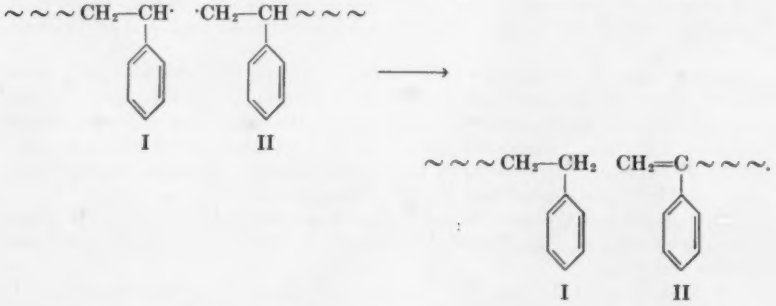


If we remember also that in the mechanical processing of a polymer the ruptures of the polymer chain may occur at different points in the macromolecule, it becomes obvious that not only macroradicals but also biradicals can be formed.

These macroradicals can take part in the following reactions:

1. Recombination (Radicals I and II come together again).
2. Combination (two fragments coming from different macromolecules come together. We get the combinations, e.g., I + I or II + II).
3. Saturation with reaction partners (system derived radical acceptors, etc.).
4. Disproportionation.

At the same time there is a possibility of deactivation by reactions without alteration in the chain length, e.g., by hydrogen transfer between two radicals with the formation of double bonds:



As well as the macroradicals produced by mechanochemical breakdown there are still present in the system large amounts of nonactivated macromolecules. As a result great importance attaches to chain transfer acts and reactions of breakdown of macromolecules under the action of radicals (which Berlin has called reactions of initiated breakdown):

in addition to the combination processes.

In assessing the reaction capacity of the macroradicals we must take into account the big effect of steric hindrance, brought about by the presence of side groups and branchings, or else by the low probability of encounter between the active atoms situated at the ends of the macromolecules.

Prompted by the work of Baramboïm and Berlin and also by the investigations of Henglein[11] on the detection of the macroradicals formed during ultrasonic breakdown, we attempted to trap and detect the macroradicals to be expected from the breakdown of Polystyrol BW (polystyrene produced by VEB Chemische Werke Buna, Schkopau) by vibromilling.

VIBROMILLING

The principle of the vibromill is that a milling vessel oscillates upon a circular track, whose plane lies parallel to the front walls of the vessel. By suitable choice of angular velocity (speed of rotation, number of rotations) and radius of oscillation (amplitude) the constituents in the mill are excited by the oscillat-

ing walls of the vessel into a periodic projection motion, so that the charge is subject mainly to the impact effect of the balls.

For the polystyrene we used a "Vibratom" ball mill manufactured by Siebtechnik GmbH, of Mülheim (Ruhr). In this apparatus (Figure 1) four porcelain barrels each holding 4 to 4.5 l are oscillated on circular tracks with a radius of 1.75 mm and a number of rotations, 1450 rpm, to suit this amplitude. The amplitude and number of rotations are not variable.

The material, Polystyrene BW, is a thermal polymer for which the makers quote an osmotically measured average molecular weight of 160,000 to 180,000 and a K value of 68.

For the experiments on detection of macroradicals only such products may be used as are free from initiator and emulsifier, otherwise side-processes occur which cannot be left out of consideration.

As a radical acceptor we used NO, produced in a Kipp apparatus from KNO_2 and H_2SO_4 and then dried and purified with H_2SO_4.

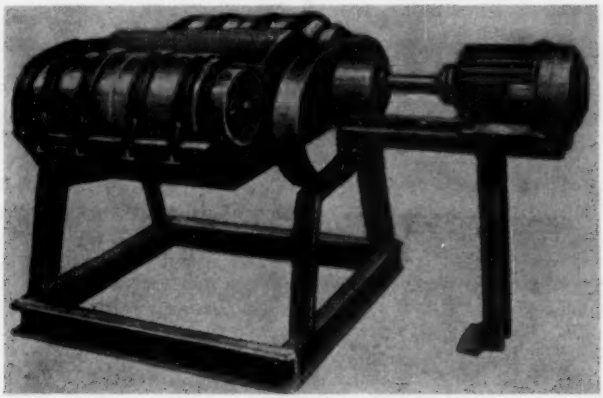


FIG. 1.—The vibromill.

At this point it seems necessary to give some notes on the carrying out of the milling. It is to be remembered that oxygen is a disturbing factor even in traces, being one of the most powerful radical acceptors. The same applies to the presence of moisture. Accordingly these two factors interfering with the detection of macroradicals are to a considerable extent eliminated by repeated evacuation of the vessles and flushing with pure nitrogen, and by drying of the charge in vacuo over P_2O_5 at about 50° C.

In order to establish the effect of the radical acceptor, parallel tests were carried out under pure nitrogen.

In each case 20 g of the polystyrene (ground down to particle size about 1 mm) were vibromilled up to 36 h with 4 kg of porcelain balls (diameter 20 to 22 mm), that is to say a charge ratio of 0.5%. The nitrogen millings took place under a slight excess pressure of 0.5 atm, while the NO millings were carried out at the pressure generated in the Kipp apparatus. The NO specimens had a slight yellow color. The adsorbed NO was removed in a vacuum drying cupboard (8 h, at 20 to 30° C). Infrared spectroscopic investigations showed that adsorbed NO could not be detected on the products thus treated.

PRODUCTS OF VIBROMILLING

Detection of nitrogen.—An approximate calculation was carried out first to decide the number of points of rupture to be expected and the number of resulting macroradicals. The number of points of rupture per molecule was calculated according to the following equation.

$$X = \frac{DP_0}{DP_1} - 1$$

DP_0 being the starting product, DP_1 the middle product, and X the number of ruptures per molecule.

The number of ruptures is thus $R = 2X$.

With complete saturation of the radicals with NO the nitrogen content in the milled product would be about 0.015% after two hours milling under NO and would rise to 0.27% after 36 hours milling. These small amounts of nitrogen are extremely difficult to determine quantitatively, and we cannot count on complete saturation of the radicals so that the nitrogen amount is considerably lower even than this. We therefore used the benzidine-copper acetate method, whose limiting concentration is $1:1.4\cdot10^{-6}$, as being an exceptionally sensitive method of determination. With this method nitrogen was definitely identified in all the NO milling specimens, while it was not detected in the samples milled under nitrogen. It was thus established that NO had reacted with the milled product.

Viscometric measurements.—For all the milled specimens we carried out viscometric measurements in 0.5% benzene solution, taking into account the humidity and ash values. An Ubbelohde viscometer with capillary I was used at 20° C.

From the determined efflux times and taking into account the Hagenbach correction factor[22] we calculated the viscosity index $Z\eta$ according to the equation of Schulz and Blaschke[23]. It we plot these $Z\eta$ values as a function of the milling time, we get the typical breakdown curves shown in Figure 2.

From this it is evident that breakdown in NO proceeds more rapidly than in N_2. It may be concluded that a proportion of the resulting macroradicals has been stabilized by the NO and thus had less opportunity for recombination or combination than in nitrogen.

K-Values According to Fikentscher Starting Product: Polystyrol BW, *K*-Value 68

Duration of milling, hours	N_2 milling *K*	NO milling *K*
2	52.5	50.7
4	47.5	45.3
8	43.0	35.7
16	29.3	26.2
24	26.7	23.0
36	19.5	17.2

In order to make a further estimate of the degree of breakdown, the *K* values according to Fikentscher's method[24] were determined.

Provided that the Staudinger viscosity remains valid for the 36 h milled polymer, we can estimate from the $Z\eta$ value a breakdown from an average molecular weight of 170,000 to about 14,000 in N_2 and to about 11,000 in NO.

Here we need mention only briefly that the melting point of the products of

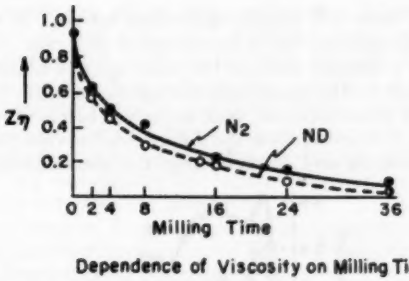


FIG. 2.—Dependence of viscosity index Z_η upon the duration of milling.

milling fell regularly corresponding to the breakdown (from 182 to 117°) and show a distinct difference as between NO and N_2.

Ultraviolet spectra.—For recording the extinction curves in the wavelength range 250 mμ to 340 mμ we used the VEB Carl Zeiss Jena Universal spectro-

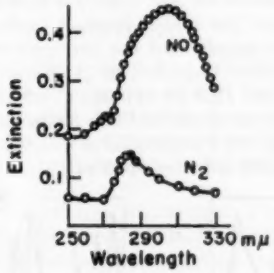


FIG. 3.—Extinction curves after 16 hours milling in nitrogen and in nitric oxide.

photometer with a 052 rock salt prism and a MVSB photocell. All measurements were carried out with 0.05% centrifuged benzene solutions of the milled specimens in quartz cuvettes of 30 mm length.

The extinction curves determined on all the milled specimens have without exception the shapes shown in Figure 3.

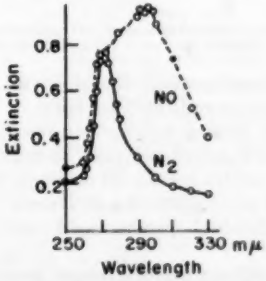


FIG. 4.—Extinction curves of 0.05% carbon tetrachloride solution (16 h), nitrogen and NO milling.

As may be seen, these is a distinct difference between NO and N_2 milling. The lower curve (N_2 milling) has a maximum at 282 mμ. The upper curve (NO milling) shows a distinct shift of the maximum to about 306 mμ, which should be attributable to the macroradicals saturated with NO.

Experiments with other solvents, such as carbon tetrachloride (Figure 4) or cyclohexane (Figure 5) likewise show the differences between the two millings—a shifting of the maximum and different height of the extinction.

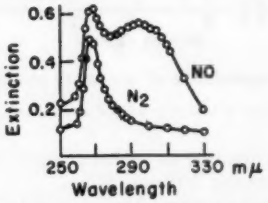


FIG. 5.—Extinction curves of 0.05% cyclohexane solution (16 h), nitrogen and NO milling.

From these measurements we may conclude that a reaction must have taken place between the NO and the milled product (macroradicals).

Infrared spectra.—To supplement the previous results, the infrared spectra of the milled specimens were recorded, by A. Klein. The measurements were carried out with the Soviet IKS 11 apparatus, on thin films of the milled products (Acknowledgments are made to Prof. Klare and Dipl. Phys. Ruscher and Schmolke of the Institut für Faserstoff-Forschung, Teltow-Seehof for help in producing and assessing the infrared spectra).

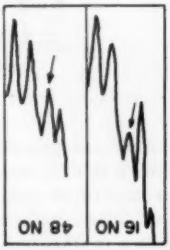


FIG. 6.—Infrared spectra of NO millings at 7.82 μ.
FIG. 7.—Infrared spectra of NO milled polymer at 6.4 μ.

The purpose of these investigations was above all to establish the bond between the NO and the macroradical. In spite of very great experimental difficulties we succeeded in getting satisfactory results.

In the spectra for the NO milled polymer, as compared with the pure polystyrene spectrum and the spectra for the N_2 millings, there occur two additional bands at 7.82 μ and at 6.4 μ. Figures 6 and 7 show juxtapositions of sections from the spectra of the individual specimens, likewise indicating an increase in intensity.

In the 7.82 μ range we did not find a stronger band either with nitrobenzene or nitrotoluene. Indeed we see quite a strong absorption minimum. Comparative measurements showed also that aromatic nitro bands do not occur

7.82 μ with nitrobenzene or nitrotoluene-benzene mixtures. According to Bellamy[25] the band at 7.82 μ is to be attributed to an extraordinarily strong NO_2 valency oscillation for compounds of the R—NO_2 type, where R is an aliphatic radical. From this it is concluded that in NO milling a number of macroradicals, increasing with the duration of milling, are saturated with NO, the adduct then being oxidized to an NO_2 derivative by the after treatment of the milled products—particularly in the production of the thin films.

On the other had on assessing the experimental results as a whole we must ascribe the band at 6.4 μ to ring nitration.

For this the radicals of Type I might be held responsible. In this type of macroradical the free electron is involved into the mesometric resonance of the nucleus, so that ring nitration is favored.

In summary we can say that there occur both nitration on the ring (radicals I) and also, proportionally to the duration of milling—radical saturation by NO (radicals II). At present we cannot make any statements as to the relative extents of the two reactions. Nevertheless the question put at the beginning of this section can be given a positive answer. A chemical bond between NO and the milling product is indicated, even if at the same time an unexpected phenomenon, that of ring nitration, has occurred.

SUMMARY

The investigation presented here, including detection of nitrogen, the viscometric investigation, melting point determinations, the ultraviolet and infrared spectra, allow of the qualitative statement that macroradicals are formed in the mechanochemical breakdown of polystyrene by vibromilling. The slight differences between N_2 and NO milling may be ascribed in part to a more rapid deactivation of the radicals.

On the foundation of the existing knowledge of mechanochemistry there result interesting prospects for science and technology, e.g., the use of macroradicals as polymerization initiators and as active types of block copolymers and graft polymers by reactions both with monomers and with macroradicals of other polymer materials.

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ABRASIVE WEAR RESEARCH ON RUBBER *

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In addition to such applications as in packings, damping elements and hose, rubber is utilized for parts which are exposed to abrasive wear, e.g., chutes, rebound plates, linings for sand blasting equipment, hopper sieves. These applications call for testing methods which allow the comparison of various rubber types among one another and also with other materials, especially with steel. The order of performance of the same material in various test methods may be different[1,2]. Therefore, in order to obtain a comprehensive picture of the abrasion resistance of a particular material, it is necessary to employ various testing methods.

TABLE I

INVESTIGATED MATERIALS

Material		Sp. G., g/cm³	Shore hardness (DIN 53505)	Vickers hardness, kg/mm²	Impact elasticity, %	Tensile strength, kg/cm²	Elong. at break, %
Notation	Type						
Rubber 1	Perbunan	1.42	88 + 90	—	18	160	180
Rubber 2	Buna	1.38	82 + 86	—	30	100	250
Rubber 3	Buna	1.25	70 + 74	—	36	125	275
Rubber 4	Perbunan	1.26	76 + 80	—	23	179	239
Rubber 5	Perbunan	1.18	58 + 63	—	45	119	342
St 37	—	7.85	—	110	—	3700 to 4500	25

This problem was clarified by the application of tests to various types of rubber, and as a comparison to malleable steel. Sliding or tangent abrasion tests include the abrasive paper method and the abrasion cup method, whereas, sand blasting abrasion tests include those on plates and those in tubing or hose. The specific gravity and the hardness of the materials under investigation are represented in Table I. The abrasive materials employed were quartz sand and river sand (Neckar sand). Details on the grain size, grain shape, major constituents and on the hardness are contained in Table II.

TESTING EQUIPMENT AND TESTING CONDITIONS

Sliding or tangent abrasive tests by means of the abrasive paper method were conducted on a stroke abrasion machine under adaptation of DIN 53516 and DIN 50330[3,4] (Figure 1). A weighted, cylindrical (10 mm diameter) testpiece is attached to a vertical, free moving sample holder, which moves back and forth horizontally. The test surface should be parallel to the surface of the abrasive paper. Furthermore, the table to which the abrasive paper is at-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Franz Widmer from an article in *Zeitschrift des Vereines Deutscher Ingenieure*, Vol. 96, pages 43–47, No. 2, Jan. 11 (1954).

TABLE II

EMPLOYED ABRASIVE MATERIALS

Type	Coarseness, mm	Shape	Major constituents	Vickers hardness, kg/mm²
Quartz sand	> 0.2 < 1.5	sharp edges	pure ground quartz	1290
Sand from the Neckar river	<3	roundish grains	lime, feldspar, quartz	cannot be determined

tached by a clamping mechanism, is rotating normal to the direction of the stroke of the sample. The testing conditions have been summarized in Table III.

Gliding abrasion tests by means of the abrasion cup method are conducted on the apparatus[5] shown in Figure 5. The sample (diameter $d = 25$ mm) is attached to a perpendicular axis and it rotates in a beaker which is filled with sand. The sample axis is eccentric with respect to the beaker axis (Figure 3). The beaker rotates considerably slower than the sample. The sample, which has the shape of a rubber hose, is slipped over a steel mandrel and held in place

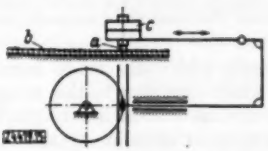


FIG. 1.—Diagram of the sliding abrasion machine; *a* test sample, *b* abrasive (abrasive paper), *c* load (weights).

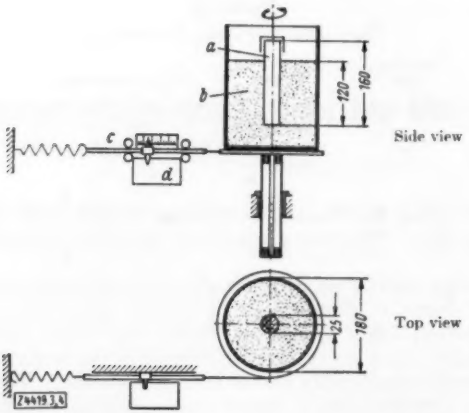
by an adhesive. The tolerance of the rotational motion at the lower end of the sample is $\leqq 5/100$ mm. The testing conditions are summarized in Table IV.

Sand blast abrasion method.—Blast abrasion on the surface of a solid body takes place either by a frequently repeated impact of individual solid particles or by the change of the impulse of a closed current (stream, flow pattern) of particles. The mode of abrasion is a function of the incident angle[6,7]. The types of abrasions which may occur are classified as follows: tangent blast abrasion, inclined (or angle) blast abrasion and rebound (or normal) blast abrasion[1], which are illustrated by Figures 4 to 6. The rebound blast abrasion values and the inclined blast abrasion values are obtained by directing the

TABLE III

TESTING CONDITIONS FOR THE ABRASIVE PAPER METHOD

Conditions \ Test material		Rubber 1 to 5, St 37 (see Table I)
Abrasive		flint paper
Coarseness of the abrasive		120 80 60 40
Pressure on sample	kg/cm²	0.325 0.75 0.5 1.0
Mean speed	m/sec	0.25
Travelled path	m	147
Stroke (single)	mm	105
Advance normal to the stroke motion	mm/m trav. path	0.413
Advance path	mm	61
Sample diameter	mm	9.9 ± 0.1
Sample surface	mm²	77



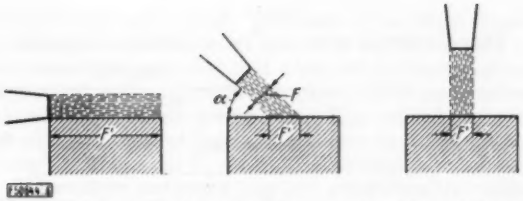
FIGS. 2 and 3.—Diagram of the abrasion cup tester; *a* test sample, *b* sand, *c* device for measuring frictional forces, *d* recording cylinder (drum). The upper figure is the side view and the lower the top view.

blast against plates (or discs) which are made from the test material. The determination of tangent blast abrasion is the most difficult. This may be achieved indirectly by extrapolation of inclined blast abrasion values[1], and also by the use of results from tangent abrasion tests. The blast abrasion experiments were performed with a sand blasting apparatus of the Gary type[1] (Figure 7). The abrasive particles are carried by a stream of pressurized air and are forced through nozzle *c* (diameter = 18 mm) against sample *d*. The blast pressure is measured immediately before the air stream enters orifice *a*. The sample discs have a diameter of 58 mm and a thickness of 10 mm. The disc is held in place by holder *f*, which rotates at a rate of 24 rpm. The holder is built in such a manner that any blast angle from 90° to 15° may be chosen. The axis of the sample is 12 mm off center with respect to the nozzle. The distance between the center of the sample and the nozzle is 60 mm. In those

TABLE IV

TEST CONDITIONS FOR THE ABRASION CUP METHOD

Materials		Rubber 1 to 5, St 37 (see Table I)
Abrasives		Quartz sand and river sand (see Table II)
Motion Data		
Sliding speed of a sample of 25 mm diameter	m/sec	1.85
Relative speed of sample center with respect to the abrasive	m/sec	about 0.01
Eccentricity *e* (distance of sample axis from cup axis)	mm	30
Duration	min	25
Traveling path of sample	km	2.8
Immersion depth of the sample in the abrasive	mm	120



FIGS. 4 to 6.—Blast abrasion types; α, incident angle; F, cross section of the sand blast; F', blasted surface of sample; $F' = F/\sin\alpha$. *Figure 4*: Tangent blast abrasion; *Figure 5*: angle blast abrasion *Figure 6*: rebound blast abrasion.

cases where hoses or tubing have to be tested, they are substituted for nozzle *c* and held in place in front of orifice *a* by means of coupling *b*. The tubes have a length of 150 mm and an inner diameter of 18 mm. The inner diameter of the orifice is 17.5 mm. In order to give stability to the rubber hose, they are glued to the inside of steel pipes. The testing conditions are summarized in Table V.

Abrasion scale.—The abrasion values determined were (1) rate of abrasion and (2) abrasion in mm/km, i.e. the decrease of the thickness after an abrasion path of 1 kilometer. According to DIN E 50321 the rate of abrasion in mm/h is the decrease of the thickness of a significant spot on the test sample, which after one hour is measured normal to the abraded surface.

It is advantageous to use relative values rather than the absolute abrasion data. Abrasion is compared with that of a standard material (steel St 37), whose abrasion values have to be determined at frequent intervals. Relative abrasion is the ratio of the abrasion volume of the subject material to the abrasion volume of St 37. Such a representation of data allows the comparison of results which have been obtained by various abrasion test methods.

RESULTS

Abrasive paper method.—The volume abrasion of rubbers by far exceeds the values of steel St 37, as shown in Figure 8. The decreasing order of perform-

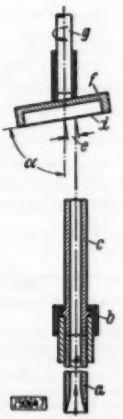


FIG. 7.—Sand blasting apparatus; *a* orifice, *b* coupling, *c* nozzle (an interchangeable tube), *d* disc shaped sample, *e* eccentricity, *f* sample holder, *g* driving shaft, α incident angle.

TABLE V

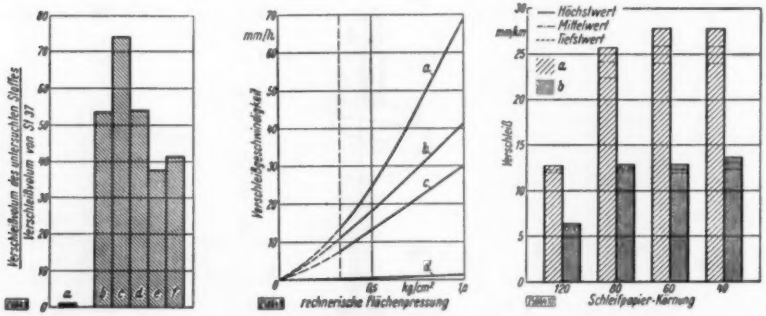
TEST CONDITIONS FOR THE BLAST ABRASION METHOD

		Tests with			
		Discs			
		Various blast angles		Various blast pressures	
		Rubber type (see Table I)			Tubes
		1 to 5		5	1 and 3
Blast angle	degrees	90 60 30 15		90	
Duration	min	2 (steel) 2 to 15 (rubber)			30
Blast pressure before orifice	kg/cm²	3		1.2 2 3 4 and 5	3

ance of the various rubber types is 4, 5, 1, 3 and 2. Figure 9 shows that over the investigated range the abrasion increases more than just linearly as the pressure is increased.

Also the effect of the abrasive paper coarseness (120, 80, 60 and 40) on the abrasion was investigated. For these experiments rubber types 2 and 4 were used, because they were most different in the sliding abrasion test (Figure 10). According to these tests, the abrasion for both rubber types with abrasive paper 120 was only half as large as with papers 40, 60 and 80. The abrasion of both rubber types with the various papers changed in the same proportions.

Abrasion cup tests.—The abrasion of the rubber types and of St 37 is greater with river sand than with quartz sand (Table VI). Using St. 37 as a standard, the relative abrasion values which are obtained with quartz sand, lie between 6.1 and 9.9, and with river sand between 5.1 and 10.2. The order of performance of the rubbers with quartz sand and with river sand is the same as in the abrasive paper test.



FIGS. 8 to 10.—Evaluation of abrasion according to the abrasive paper method. *Figure 8*: Relative abrasion of the five rubber types referred to Steel St 37 according to Table I. Abrasive: flint paper, coarseness 80; calculated surface pressure, 0.5 kg/cm². *a* St 37, *b* Rubber type 1 (Shore hardness 88), *c* Rubber type 2 (Shore hardness 85), *d* Rubber type 3(Shore hardness 72), *e* Rubber type 4 (Shore hardness 77), *f* Rubber type 5 (Shore hardness 62). *Figure 9*: Influence of the computed surface pressure (the abscissa) on the abrasion rate (the ordinate). Abrasive: flint paper, coarseness 80. *a* Rubber type 2, *b* Rubber type 1, *c* Rubber type 4, *d* Steel St 37. *Figure 10*: Influence of the flint paper coarseness (the abscissa) on abrasion (the ordinate). Calculated surface pressure, 0.5 kg/cm². *a* Rubber type 2, *b* Rubber type 4. With sand paper 120 the abrasion was only about half as large as with papers 40, 60 and 80.

Blast Abrasion Tests with Discs. Influence of the Blast Angle.—The blast abrasion V_α is composed of sliding abrasion $V_{\alpha G}$ and of rebound abrasion $V_{\alpha P}$. Blast abrasion research[8] has shown, that when the incident angle α is increased, a material-dependent angle is reached, beyond which only rebound abrasion occurs and the sliding abrasion disappears. This critical angle may be determined graphically by means of a plot of incident angle versus blast abrasion. In Figure 11 the blast abrasion V_α for St 37 is plotted as a function of the incident angle. Since under the prevailing test conditions the surface F' on the test sample which is abraded by a sand blast of cross section F (Figure 5) becomes smaller as angle α is increased and the blast density increases, it would appear that also the abrasion for equal surfaces should increase. However, the experiments have shown, that for angles between 60° and 80° the abrasion decreases. This reversion becomes even more distinct, when the abrasion values are calculated for equal specific blast densities ($V'_\alpha = V_\alpha : \sin\alpha$; see curve V'_α in Figure 11). If the impulse P for the impact of a sand particle is assumed to be constant, whereas the incident angle α may change, the rebound abrasion

TABLE VI

RESULTS OF THE ABRASION CUP TESTS. RATIOS OF THE ABRASION VALUES[a] WITH RESPECT TO ST 37

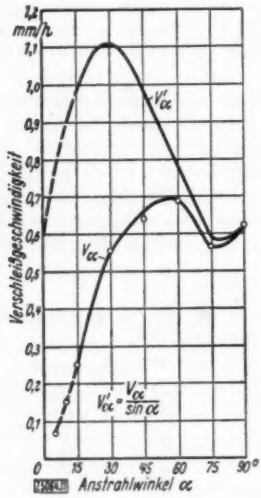
Test material \ Abrasive	Quarts sand			River sand		
	High value	Low value	Mean value[b]	High value	Low value	Mean value[b]
Rubber 1	8.1	6.6	7.2	9.1	6.9	7.9
Rubber 2	11	8	9.9	11	8.2	10.2
Rubber 3	9.3	6.9	8.3	9.5	7	8.5
Rubber 4	6.7	5.2	6.1	5.3	4.5	5.1
Rubber 5	7.2	5.9	6.8	5.4	4.8	5.5
St 37	—	—	1	—	—	1

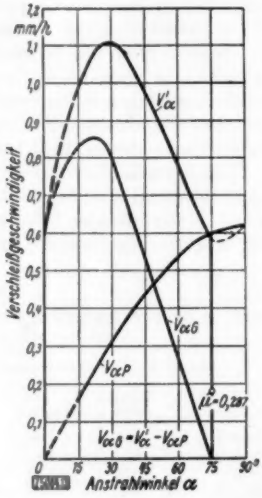
[a] Abrasion of St 37 with quarts sand: $5.7 \cdot 10^{-4}$ mm/h $\triangleq$ $0.9 \cdot 10^{-3}$ mm/km.
Abrasion of St 37 with river sand: $13.3 \cdot 10^{-4}$ mm/h $\triangleq$ $2.0 \cdot 10^{-3}$ mm/km.
[b] Mean value from 5 to 6 determinations.

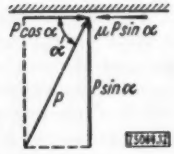
$V_{\alpha P}$ becomes a function of $P \cdot \sin\alpha$ and the sliding abrasion $V_{\alpha G}$ becomes a function of $P(\cos\alpha - \mu \sin\alpha)$, and of $(\sin\alpha, \cos\alpha)$, Figure 12. For values of $\cos\alpha \leqq \mu \sin\alpha$, the sand particle no longer can slide on the test surface. Therefore sliding abrasion no longer occurs, i.e. rebound abrasion exclusively takes place even at incident angles which are less than 90°, and the blast abrasion for angles ranging from the critical angle to 90° is a function of $P \cdot \sin\alpha$. Applying these assumptions, the rebound abrasion was measured for $\alpha = 90°$, and from this value the other values of $V_{\alpha P}$ were obtained by multiplication with $\sin\alpha$. These values were entered in Figure 13. For large incident angles these operations are providing the shape of curve V'_α and also the critical angle (in this case 74°). The curve of the sliding abrasion $V_{\alpha G}$ is obtained by subtracting the ordinates of $V_{\alpha P}$ from V'_α. The determination of the friction coefficient μ by means of the equation $\cos\alpha = \mu \sin\alpha$ gave the following value: $\mu = \operatorname{ctg}\alpha = 0.287$.

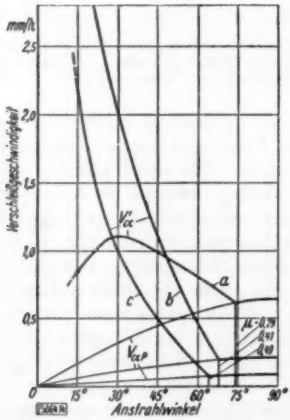
The abrasion values V'_α and $V_{\alpha P}$ of rubber types 1 and 3, as well as those of St 37 were plotted versus the blast angle, as represented in Figure 14. The friction coefficients μ of both rubber types are larger than the coefficient of St 37. For rubber type 1: $\mu = \operatorname{ctg}\alpha \approx 0.41$ ($\alpha = 68°$); for rubber type 3: $\mu = \operatorname{ctg}\alpha \approx 0.49$ ($\alpha = 64°$). In comparison to St 37 the range over which only rebound abrasion occurs is larger because the friction is relatively large.

The abrasion of both rubber types by blast mechanisms is smaller than the abrasion of steel. This may be related to the long range elasticity of rubber: The impulse of a sand particle on the rubber sample is distributed over a longer path and the speed eventually is lower. Therefore, the maximum force which



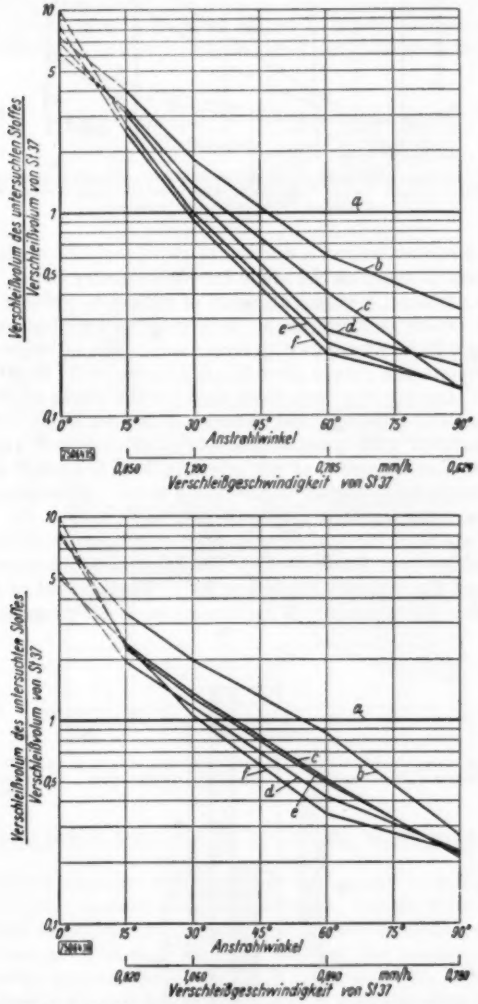






FIGS. 11 to 14.—Blast abrasion of discs by the sand blasting apparatus as a function of the blast angle. Test material: St 37 (Vickers hardness 128 kg/mm²) and rubber types 1 and 3. Abrasive: quartz sand, grain size >0.2 <1.5 mm. Blast pressure: 3 kg/cm². *Figure 11*: blast abrasion of St 37. V_α measured blast abrasion; V_α' specific blast abrasion (i.e., calculated for equal blow densities). The abscissa is incident angle and the ordinate abrasion rate. *Figure 12*: The force (or impulse, resp.) which occurs during blast abrasion, is broken down into its components corresponding to the rebound and sliding abrasion. P = Force (or impulse, resp.) of an abrading particle. *Figure 13*: determination of pure sliding abrasion $V_{\alpha G}$ as the difference between the specific blast abrasion V_α and rebound abrasion $V_{\alpha P}$. μ = friction coefficient. The ordinates for Figs. 13 and 14 are abrasion rate and the abscissas are incident angle α. *Figure 14*: blast abrasion V' and rebound abrasion $V_{\alpha P}$ of 2 rubber types and of steel St 37. *a* St 37, *b* rubber type 1, *c* rubber type 3. Fig. 11 is upper left, Fig. 12 is lower left, Fig. 13 is upper right, and Fig. 14 is lower right.

is responsible for the abrasion of rubber is comparatively smaller than that for steel. With decreasing incident angle and consequently with increasing contribution of sliding abrasion, the blast abrasion of both samples rapidly increases. The abrasion curve of St 37 which at first runs in the same direction



FIGS. 15 and 16.—Ratio of the blast abrasion values (volumes) of rubber discs with respect to steel St 37 as a function of the blast angle. Blast Pressure: 3 kg/cm². The values for blast angles ranging from 15° to 90° have been obtained with the sand blasting apparatus. For the blast angle of 0°, the results of the abrasion cup tests were used because the blast abrasion test does not function at this angle. *a* St 37, *b* rubber type 1, *c* rubber type 4, *d* rubber type 5, *e* rubber type 2, *f* rubber type 3. *Figure 16*: Test results with quartz sand (size >0.2 <1.5 mm). The scale below the abscissa shows the abrasion rates of St 37 (mm/h) for corresponding blast angles. The ordinate is relative abrasion (to St 37) and the abscissa is incident angle. *Figure 16*: test results with sand from the Neckar River (size <3 mm). The scale below the abscissa and the coordinates is the same as for Fig. 15.

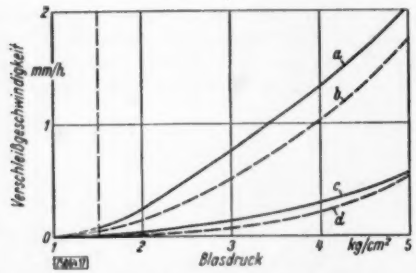


FIG. 17.—Abrasion versus blast pressure for a incident angle of 90°. Abrasive: quartz sand and river sand
a St 37 with river sand, *b* St 37 with quartz sand, *c* Rubber Type 5 with river sand,
d Rubber Type 5 with quartz sand.

as the curves for rubber, shows a maximum at an incident angle of about 30°, but then it decreases again as the angle becomes smaller.

The relative abrasion (volume abrasion of rubber to volume abrasion of St 37) are plotted versus incident angle: in Figure 15 for abrasion with quartz sand and in Figure 16 for abrasion with river sand. The ordinate is logarithmic. In order to complete the curves over the full range of 0° to 90°, the relative abrasions of the abrasion cup tests were used for the angle of 0°. Figures 15 and 16 show that the pure rebound abrasion (incident angle = 90°) is rather small when compared with pure sliding abrasion (incident angle = 0°). It can also be seen that the order of performance with the blast abrasion test is different from the order in the sliding abrasion tests. (Compare the intersecting curves between the incident angles 0° and 15°.)

Influence of the blast pressure during rebound abrasion.—Experiments were performed on rubber type 5 and St 37. The blast pressure varied between 1.5 and 5 kg/cm² and the incident angle was 90°. The amount of sand used was the same for each experiment. With increasing blast pressure the abrasion

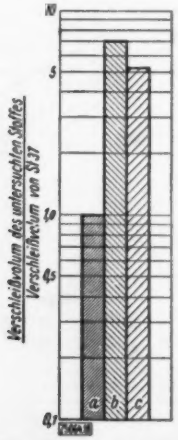


FIG. 18.—Test results on pipes with quartz sand. *a* St 37, *b* Rubber Type 1, *c* Rubber Type 3. The ordinate is relative abrasion (to St 37).

increases as shown in Figure 17. Abrasions are generally somewhat larger with river sand than with quartz sand.

Blow abrasion tests with pipes.—Results of blast abrasion tests with tubes made from rubber types 1 and 3 with quartz sand as abrasive are shown in Figure 18. The blast abrasion rate of St 37 is about 0.720 mm/h. Comparison of the relative abrasions with those of Figure 15 shows that the test conditions in a tube are equivalent to those obtained on a disc with an incident angle of 5°.

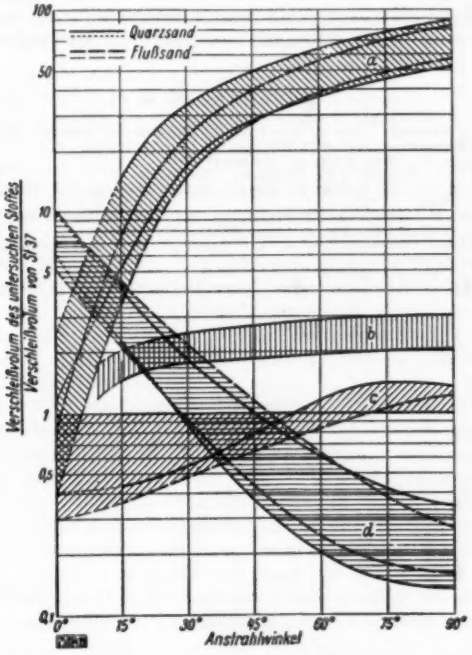


FIG. 19.—Blast abrasion of various materials as a function of the blast angle. Abrasive: quartz sand and river sand (Fluss sand). Blast pressure: 3 kg/cm². *a* melted basalt, *b* non-alloyed hard castings, *c* forged steels, *d* rubbers.

ABRASION BEHAVIOR OF OTHER MATERIALS

Figure 19 shows abrasion values which were taken from Figure 15 (cross-hatched horizontally, section d). Furthermore, results from similar experiments with other materials are represented; basalt, malleable steels and non-alloyed hard castings. In each case the ratio of the volume abrasion of the test material to the volume abrasion of St 37 has been used. This figure clearly shows that rubber is a much better construction material than other materials, when rebound abrasion predominates. The relationships for predominantly sliding abrasion are quite different. Under such conditions rubber is by far inferior to other materials. The experimental abrasion values are valid only for dry sand. Recent investigations have shown, that rubber and rubberlike materials perform better when moist sand is used.

SUMMARY

The abrasion resistance of five different types of rubber were compared with steel (St 37) by various testing methods, such as the abrasive paper method, the abrasion cup method and the sand blasting method. The order of resistance of the various types of rubber against sand blasting is different from the order which is obtained with the sandpaper and abrasion cup methods. However, variations of the testing conditions within one method generally does not change the order. It has been shown, that rubber is more resistant against sand blasting than other materials investigated (basalt, malleable steel, non-alloyed hard castings) if the sand blast is directed essentially perpendicularly against the tested surface.

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MOLECULAR BASIS FOR THE MULLINS EFFECT *

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INTRODUCTION

The physical phenomena now widely known as the "Mullins effect" was apparently first studied in detail by Holt[1] in about 1930. He showed that if a vulcanized rubber which contains carbon black is stretched to a relative elongation $\alpha_m = L/L_0$ and released, it will not follow the same stress-strain curve when it is stretched once again to this same elongation. Instead, the rubber appears much softer on the second stretch for elongations below α_m.

Holt examined this behavior in some detail and showed that additional prestretches to α_m softened the rubber further, but to a lesser degree than was observed on the first prestretch. In addition, Holt showed that the rubber regains a portion of its stiffness if allowed to rest in the relaxed state. Although this recovery was very slow at room temperature, up to about 50% recovery was noted after about an hour at 100° C. Similar softening effects were noted in gum stocks at exceedingly high elongations, but the effects were much less marked than in the filled stocks.

This same effect was examined in more detail by Mullins[2,3] after 1940. His results confirmed and greatly extended the earlier results of Holt. In addition, Mullins speculated about the mechanisms involved but came to no definite conclusion in that regard. Later[3], however, he and Tobin presented a phenomenological theory for the effect wherein they considered the rubber to be composed of hard and soft regions. They showed that their data could be described by assuming that some fraction of the hard regions became soft after a prestretch. No definite molecular basis for this process was proposed by Mullins and Tobin, although they speculated that either the breaking up of filler particle aggregates or the breaking loose of rubber to filler bonds might be involved.

Later work by Blanchard and Parkinson[4,5] confirmed and extended the data of Holt and Mullins. Further, these authors concluded that the softening was due to the breaking of rubber to filler bonds. They incorporated this idea into a semiempirical theory which agreed with their experiments. In addition, they obtained what they believed to be a distribution for the strength of the rubber-filler bonds. It will be seen in that which is to follow that their distribution probably does not represent what they thought it did, even though their basic ideas were correct.

MOLECULAR PICTURE

Consider the rubber molecules to be bound to the filler at certain sites on the filler surface. If the surface area of the filler in square centimeters is S per

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cubic centimeter of rubber compound and the average surface area per chain attachment is σ square centimeters, the number of attached chains will be (S/σ) per cubic centimeter of compound.

When the rubber is stretched to a relative elongation α, the distance between centers of the filler particles will change by the same factors. This means that we assume the positions of the filler particles will undergo an affine deformation. Since the particles are quite large in comparison to atomic dimensions one would expect that even at very large stresses the unbalanced force on any given particle will be unable to move it far through the rubber matrix. Consequently, the assumption of an affine deformation of the filler particle positions should be valid.

Suppose Figure 1 represents three rubber chains attached to two filler particles before a force is applied to the rubber. If the rubber is now stretched in the horizontal direction to a relative elongation α, the particles must separate so that the distance between centers is now α times larger than the previous

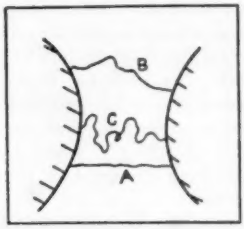

FIG. 1.—Three typical chains attached to two adjacent filler particles.

value. If α is appreciable, chain A must rupture. Chain B might rupture if α is sizeable. Chain C will not rupture unless the value of α is quite large. Obviously, the word "rupture" should not be taken to mean that the break occurs in the chain itself. The chain may merely pull loose from the filler surface, instead.

In any event, if the rubber is allowed to retract to its initial value and is restretched, it will appear softer, since the chains which broke are no longer resisting deformation. Consequently, the Mullins effect would be observed. We will show in the quantitative calculation given in this report that this process gives rise to strong enough forces to explain the effect. Even though the number of such chains which break is relatively small, the tremendous force which a chain holds just before it breaks causes the effect of the small number to be easily noticed.

Before proceeding with the computation, it should be explained why a gum stock does not show this effect. The effect depends upon the fact that chains like chain A in Figure 1 must break at very low relative elongations. If chain A were merely tied to two network junction points, as would be the case in a system without filler, the network junctions would be pulled through the rubber matrix so as to keep the forces in A small. In other words, the network junctions do not undergo an affine deformation in the vicinity of a highly strained chain. As a result, chain A need not elongate much, even though the sample is deformed considerably. It will therefore not break until very high deformations are imposed on the sample, and consequently the softening effect will be very small at moderate sample elongations.

COMPUTATION

Consider a system of long polymer chains for which the effects of chain ends may be neglected. Imbedded in this polymer is a volume fraction v_f of spherical filler particles with total surface area S per unit volume. There will be certain sites on the filler surface to which a chain unit is attached, the number of such sites being N and the area per site $\sigma = S/N$.

It is necessary to know what the distribution of chain lengths is for chains attached between filler particles. This may be computed in the following way, provided one assumes gaussian chains for which the root mean square separation of two chain segments n segments apart is $(a^2n)^{\frac{1}{2}}$. We also assume that the primary molecular weight is much larger than the molecular weight between chemical crosslinks.

Suppose first that there are two parallel filler surfaces separated by a distance x. If a certain chain segment is attached to one of these surfaces, the chance that the nth segment along the chain will be within a distance Δx of the other surface is

$$(3/2na^2)^{\frac{1}{2}} \exp\{-(3x^2/2na^2)\}\,\Delta x \tag{1}$$

If the chain segments are taken to have a volume near a^3, then the chance that this segment is attached to the surface will be approximated by letting $\Delta x = a$ and multiplying Equation (1) by a^2/σ. Therefore, the chance that the nth chain segment is bound to the other filler surface is approximately

$$(a^3/\sigma)(3/2na^2)^{\frac{1}{2}} \exp\{-(3x^2/2na^2)\} \tag{2}$$

It is next necessary to take account of the fact that some segment along the chain closer than the nth may have already been attached to the surface. Since the probability that the pth segment has been attached is given by Equation (2) upon replacing n by p, one has that the chance that no prior segment has attached itself is

$$\prod_{p=1}^{n-1} [1 - (a^3/\sigma)(3/2pa^2)^{\frac{1}{2}} \exp\{-(3x^2/2pa^2)\}] \tag{3}$$

The probability that the nth segment is the first one along the chain to attach to the opposite surface is the product of expressions (2) and (3). This quantity which will be denoted as $P(n, x)$ is the probability that the chain length between filler surfaces is n when the surfaces are a distance x apart. After expanding and simplifying the product one finds

$$P(n, x) = (a^2/\sigma)(3/2n)^{\frac{1}{2}} \exp\{-y^2 - (a^2/\sigma)(n)^{\frac{1}{2}}\phi\} \tag{4}$$

where

$$y^2 = 3x^2/2na^2$$

and

$$\phi = (6)^{\frac{1}{2}} \exp\{(-y) - y(\pi)^{\frac{1}{2}}[1 - E_2(y)]\}$$

with

$$E_2(y) = (4/\pi)^{\frac{1}{2}} \int_y^\infty \exp\{-t^2\}\,dt$$

If the rubber sample of original length L_0 is stretched to length L, the relative elongation α will be L/L_0. The actual rubber between filler particles must

elongate more than this to compensate for the filler which elongates none at all. It may be shown that the relative elongation α' of the rubber between filler particles in the direction of stretch is related to α in the following way (see Appendix I):

$$\alpha' = (\alpha - v_f^{\frac{1}{2}})/(1 - v_f^{\frac{1}{2}}) \tag{5}$$

In the remainder of this report, the relative elongation inside the pure rubber will be designated by primes.

The chain which breaks at an extension ratio α_c' will be that for which $n_c a = \alpha_c' x$, where n_c is the value of n for this particular chain. One therefore has that the number of chains which have $n = n_c$ and will break at an extension ratio α_c' is

$$\sum N(x) P(n_c, x) \tag{6}$$

where $N(x)$ is the number of chains between surfaces separated by a distance x and the sum extends over all possible separations. It is clear that $N(x)$ will be a complex function involving the average surface separation, size and shape of the particles. We shall approximate it as

$$N(x) = N(\beta/b) \exp\{-(\beta^2/b^2)(x - b)^2\} \tag{7}$$

where b is an average surface separation.

The parameter β in Equation (7) determines the sharpness of the distribution. If $\beta = 0$, all separations are equally probable. If $\beta = \infty$, only $x = b$ is allowed. We shall choose β in such a way that $N(a)/N$ gives the proper probability for finding surfaces separated by a distance a, that is, nearly in contact. This particular choice is made since the following portions of the computations are most dependent upon the values at small surface separations. It is easily shown in a qualitative way (see Appendix II) that for spherical particles with radii about 150 A and for which b/a is about 30, the probability of a separation less than a is of order 10^{-4}. This agrees with Equation (7), provided $\beta = 2.5$. If $\beta = 2.0$, the probability is about ten times larger, and so β is reasonably well determined from even such qualitative considerations.

The number of chains having $n = n_c$ is obtained by substituting from Equations (4) and (7) into Equation (6) and replacing the summation by an integral over x. In carrying out this integration it must be remembered that $n_c = \alpha_c' x/a$. The integral is not easily carried out without approximation. We have evaluated it by expanding the exponential, retaining only two terms of the expansion, and then expanding ϕ in series form. The resulting series is then integrated term by term after ignoring the small variation of the factors in front of the exponentials. The final result is a rather involved series. To avoid working with such a cumbersome expression, we have replaced it by the following one which fits it within the range of interest to a few per cent. The number of chains having $n = n_c$ is found to be

$$NP(n_c) = 4.75 \times 10^{-3} N(a/b)^{\frac{1}{2}}(a^2/\sigma) \exp\{4.7(a\alpha_c'/b)^{\frac{1}{2}}\} \tag{8}$$

where β has been given the value of 2.5 suggested above. The factor 4.75×10^{-3} varies inversely as β^9 and the factor 4.7 varies directly as β^2 to a good approximation for $2 \leqslant \beta \leqslant 4$.

The number of chains within range dn_c is $NP(n_c)$-dn_c. It is of more interest to know the number of chains which break within the range $d\alpha_c'$. Since the

average value of n_c is obtained by replacing x by b one has $n_c = \alpha_c'(b/a)$ from which $dn_c = (b/a)d\alpha_c'$. One therefore finds that the number of chains which break in the extension range $d\alpha_c'$ is

$$4.75 \times 10^{-3} N (a/b)^{\frac{1}{2}} (a^2/\sigma) \exp \{4.7 (a\alpha_c'/b)^{\frac{1}{2}}\} d\alpha_c' \tag{9}$$

If one is interested in the contribution of such chains to the retractive force in the rubber when the extension of the rubber is α_c', it is necessary to determine the way in which the tension in a chain varies as a function of α'/α_c'. The cor-

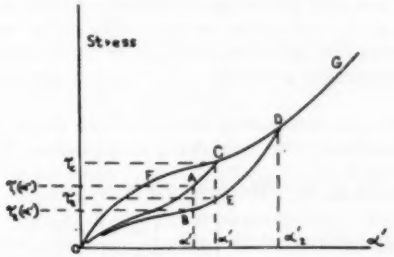

FIG. 2.—A schematic set of stress-strain curves illustrating the Mullins effect.

rect expression for the tension F in a chain which is extended to a fraction r/na of it maximum length is[9]

$$r/na = \coth (aF/kT) - (kT/aF) \tag{10}$$

This expression may be approximated in such a way that, if F_c is the tension in the chain at break, the tension at any elongation is given by

$$F = F_c(\alpha'/\alpha_c')/[(\gamma + 1) - \gamma(\alpha'/\alpha_c')] \tag{11}$$

where $\gamma = F_c a/kT$. This expression is exact at $F = F_c$ and becomes a progressively poorer approximation as F becomes smaller and as γ is decreased. For $\gamma = 100$ the correct value for $F/F_c = 0.093$ at $\alpha'/\alpha_c' = 0.90$, while Equation (11) gives $F/F_c = 0.082$. Since γ will usually be larger than 100, as will be seen later, Equation (11) should be satisfactory for the present purposes.

Not all of the N chains should be counted in computing the load being held by the sample. This is the result of the fact that only the number of chains acting across a given cross section of the sample hold the load. The remainder of the chains are essentially in series with these chains and should not be counted. Considering a sample in the form of a unit cube, any cross section will have $(1/\sigma)$ filler bound chains crossing it. Therefore, N in Equation (9) should be replaced by $(1/\sigma)$ if one is interested in the tensile forces held by the filler bound chains.

Refer to Figure 2. If a filled rubber is stretched for the first time to an elongation α_1', it will follow the stress-strain curve OFC. Upon a second stretch it will follow the curve OACD. If, after reaching point D on this curve, the rubber is again allowed to retract, it will follow the curve OBEDG on the next stretch. Using the equations derived here, we can now write down an

expression for the softening effect due to prestressing. In particular one can write an expression for $\tau_1(\alpha') - \tau_2(\alpha')$ where these quantities are defined in Figure 2.

The softening represented by the quantity $\tau_1(\alpha') - \tau_2(\alpha')$ is the result of the breaking of filler-chain bonds as the rubber was stretched from C toD during the second stretching cycle. To compute this quantity one replaces N by $(1/\sigma)$ in Equation (9), multiplies Equation (9) by Equation (11), and integrates the result, $\alpha_1' \leqslant \alpha_c' \leqslant \alpha_2'$. This process merely adds up the forces which are caused at an extension α' by filler attached chains which will subsequently break at extensions between α_1' and α_2'. Of course, if one takes α_2' to be very large and $\alpha_1' = \alpha'$, one will obtain the amount by which the rubber is stiffened at any elongation α' by the action of the rubber-filler attached chains. In practice α' should never be taken larger than the ultimate elongation in an nonfilled rubber of comparable structure, since such values of α_2' are physically impossible.

If one carries out the integration indicated one finds, upon neglecting the relatively slow variation of the exponential in Equation (9),

$$\tau_1(\alpha') - \tau_2(\alpha') = 4.75 \times 10^{-3} F_c (a/b)^{\frac{1}{2}} (a/\sigma)^2 (\gamma + 1)^{-1} \times \exp\{4.7 (a\alpha_1'/b)^{\frac{1}{2}}\} \left\{ \alpha' \ln \left[\frac{\alpha_2'(1 + \gamma^{-1}) - \alpha'}{\alpha_1'(1 + \gamma^{-1}) - \alpha'} \right] - \ln \left[\frac{\alpha_2'(1 + \gamma^{-1}) - 1}{\alpha_0'(1 + \gamma^{-1}) - 1} \right] \right\} \quad (12)$$

The second logarithm in the brackets in Equation (12) is a correction term (usually small) needed to make $\tau_1(1) - \tau_2(1) = 0$ as it must be. It is made necessary by the fact that no provision had been made in previous equations for the fact that all internal chain forces must balance out to zero when $\alpha' = 1$.

APPLICATION TO SBR

Equation (12), which should be applicable to any rubber-filler system, contains four molecular parameters, a, F_c, σ, and b. However, since the segment length a never occurs alone, the equation is completely determined by three parameters, aF_c, b/a, and σ/a. The parameter a may be evaluated from the stres-strain curve of the vulcanized unfilled rubber if so desired. This is done for the case of SBR in Appendix III, where it is found that $a = 4.3$ A. In any case, its value is not needed for the application of Equation (12).

The constants listed above may be obtained from a set of experimental curves such as those shown in Figure 2. In particular, the two curves OAC and OBD allow one to determine $\gamma = aF_c/kT$. This is done as follows.

The ratio $R = (\tau_1 - \tau_2)/(\tau_1 - \tau_E)$ may be computed from the experimental data. This ratio may also be obtained from Equation (12) by dividing Equation (12) by a similar equation in which α' is replaced by α_1'. All the unknown constants except γ disappear from this ratio, and so comparison of the experimental value for R with the theoretical value will give a numerical value for γ. It is more accurate, hower, to compute R from the experimental data at various α' values and plot these values of R as a function of α'. Assuming a value for γ, one can also plot a theoretical curve for the variation of R with α'. The value of γ which gives rise to the best agreement with experiment is the correct value.

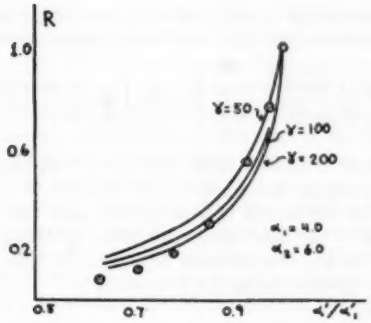

FIG. 3.—Comparison of experiment (points) and theory for the determination of γ at the γ values indicated on the curves.

This has been done for some data of Mullins[3] for SBR containing 50 parts of MPC black. The values $\alpha_1' = 8.5$ and $\alpha_2' = 13.5$ were used. These values correspond to α_1 and α_2 values of 4 and 6 respectively., The results are shown in Figure 3, where the points are from the experimental data. It is clear that the agreement between the experimental and theoretical curves leaves something to be desired. However, the upper portion of the experimental curve shown there is extremely sensitive to a small amount of permanent set which plagues this type of measurement. In addition, the upper portion of the curve will be lowered somewhat by a second extension to α_1 and so the exact experimental values in this region are in doubt. It appears that γ should be taken to be about 200, although it might possibly be as low as 100 or as high as 300. Fortunately, its exact value is not extremely critical in determining the overall shapes of the experimental curves.

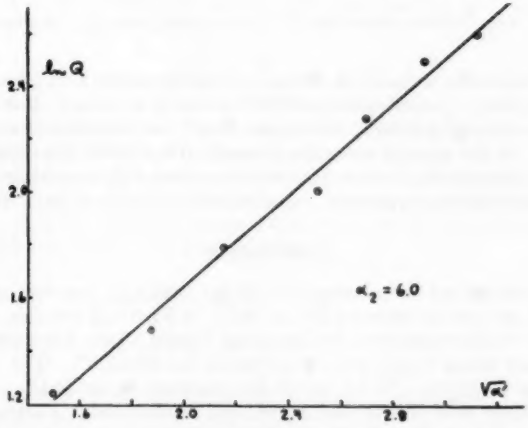

FIG. 4.—Comparison of theory (points) and experiment showing the Mullins effect in SBR loaded with 50 parts of MPC black.

The determination of a/b is best made by examining the curve OFCDG of Figure 2. From Equation (12) it is seen that, if $\phi(\alpha_1')$ is the function

$$\left\{\alpha' \ln\left[\frac{\alpha_2'(1+\gamma^{-1})-\alpha'}{\alpha_1'(1+\gamma^{-1})-\alpha'}\right] - \ln\left[\frac{\alpha_2'(1+\gamma^{-1})-1}{\alpha_1'(1+\gamma^{-1})-1}\right]\right\}$$

in Equation (12), then a plot of $\ln Q = \ln[(\tau_c - \tau_E)/\phi(\alpha_1')]$ vs. $(\alpha_1')^{\frac{1}{2}}$ will give a straight line of slope 4.7 $(a/b)^{\frac{1}{2}}$. The values of $\tau_c - \tau_E$ are obtained from the experimental curves OFD and OBED and the values of $\phi(\alpha_1')$ are obtained by setting $\alpha' = \alpha_1'$ and using $\gamma = 200$. Making use of the same experimental data as before, one obtains the straight line shown in Figure 4. The slope of this line gives a value for b/a of 29.

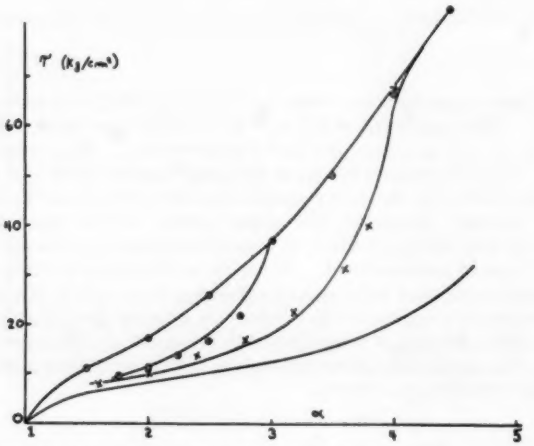

FIG. 5.—A plot of the experimental data in a form useable for the determination of b/a.

Finally, the value of (a/σ^2) is chosen so that Equation (12) gives the experimental value for $\tau_1 - \tau_2$ at some arbitrary value of $\alpha' = \alpha_1'$. For the greatest accuracy, one should probably determine (a/σ^2) for the data at a rather large value of α'. In the present case, the theoretical curve fits the experimental so well that the value of (a/σ^2) does not vary more than 6%, no matter which value of α' is selected for its evaluation. One finds that $(\sigma/a) = 10 \times 10^{-8}$ cm.

DISCUSSION

Having determined the constants γ, (b/a), and σ/a, one can use Equation (12) to plot any set of curves such as those in Figure 2 for this rubber-filler system. To test the equation, the curves of Figure 5 have been plotted. The full curves are those found from experiment by Mullins[2]. The points were obtained from Equation (12) by use of the constants found in the previous section. It is clear that substantial agreement is obtained. Furthermore, this agreement is not just a fortuitous coincidence which occurs because of our choice of the three parameters. Variation of these parameters within their limits of

error does not seriously harm the agreement found in Figure 5. Moreover, we will next show that these constants are entirely reasonable in magnitude.

First, consider the ratio b/a. If a is given the value found in Appendix II, 4.3 A, then b will equal 130 A. If one pictures the MPC black particles to be spherical with radius 125 A and placed on a cubic lattice in the rubber, the distance between their centers will be about 330 A. It would therefore appear that the value found for b, the average distance between surfaces in any one direction in the matrix, is not unreasonable.

Using the same value for a, one finds that the surface area per attachment, σ is about 44 A^2. This again is a reasonable value. Although Frisch et al.[6] have found an area of about 900 A^2 for solution adsorption of polystyrene on carbon black, and others[7, 8] have found similar values for adsorption of rubbers from solution, not too much importance should be given to these values, since there is no real reason to believe that the rubber-filler bonds discussed here are the same as in the case of solution adsorption.

The value of the strength of the weakest point in the chain may be found from the fact that $\gamma = (F_c a/kT) = 200$. This gives a value for F_c of about 2×10^{-4} dynes. It is not known what force the C—C bond can hold for an appreciable time, and so one is unable to say from this information alone whether the chain breaks loose at the filler particle or whether it breaks along the chain. The answer to this question may be determined in the following way.

Equation (10) gives the chain end displacement, r, in terms of the force applied to it. The energy stored in the chain at break is obtained by multiplying dr by F and integrating over r from $r = 0$ to the value of r at the breaking point. This is easily done, and the result for the elastic energy stored in the chain at break is

$$nkT[\ln (\gamma/\sinh \gamma) + \gamma \operatorname{ctnh} \gamma - 1] \tag{13}$$

The elastic energy per bond E_e is then

$$\begin{aligned} E_e &= kT[\ln (\gamma/\sinh \gamma) + \gamma \operatorname{ctnh} \gamma - 1] \\ &\leqq kT[\ln (2\gamma) - 1] \end{aligned} \tag{14}$$

where the approximate form is accurate to better than a few per cent for $\gamma > 10$. With $\gamma = 200$ one finds $E_e/kT = 5.0$. This is a relatively small amount of energy compared to that needed to break a C—C bond, about 60 kcal/mole, and so the effect of thermal energy must also be considered.

If a bond is to break at a temperature T in a reasonable length of time, say 10^2 sec, then the product of the bond vibration frequency, about 10^{12}, by the factor $\exp\{-E_e/kT\}$ must be about 0.01, where E_t is the thermal energy needed to break the bond. We therefore have

$$\exp\{-E_t/kT\} \leqq 10^{-14}$$

from which

$$E_t/kT \leqq 32$$

One therefore has that the bond concerned here requires an energy E to break, which is given by

$$E/kT \leqq (E_t/kT) + (E_e/kT) \cong 37 \tag{15}$$

Therefore E is about 22 kcal/mole. This is to be compared with the C—C bond energy of about 60 kcal/mole.

The above result indicates that the weak link is the attachment at the filler surface. An examination of Equation (14) shows that any reasonable value of γ will not alter the above result by much. In addition, the assumption that the elastic energy is evenly distributed along the chain is not a critical factor. It would therefore appear quite certain that the chain itself does not break but that the break occurs at the point of attachment.

The energy of the filler-rubber bond is not accurately given by the above computation, however. This is a result of the fact that Equation (14) was derived only for the rubber chain, and the bond at the filler surface will certainly not comply with Equation (10). About all one can say is that the energy needed to break this bond is greater than 20 kcal./mole or it would break by itself at room temperature. Temperature variation studies of the Mullins effect will be needed to place an upper limit on this value as well as to raise the lower limit.

At first thought it seems possible to determine the strength of the filler-rubber bond from the enclosed area of loops such as OACDEO in Figure 2, since this area is a measure of the energy lost by breaking bonds along the portion of the curve CD in Figure 2. This process is not as simple as it seems, however. Although one can easily calculate the number of chains which are torn loose from the filler, the energy loss due to these chains is not simple to interpret. First, the energy per chain is stored in the total n bonds of the chain plus the bonds at the filler surface. Although one can show that the elastic plus thermal energy per bond is less than 60 kcal, it is impossible to obtain the exact energy one should assign to the filler-rubber bond. One is therefore no better off than with the previous method of calculation In fact, it turns out that the result obtained from the loop area is much more sensitive to the exact value of γ than was the previous method. It therefore appears that the filled-rubber bond energy is not obtainable from the present data taken only at one temperature.

The present theory provides a basis for a fruitful experimental approach to the problem of rubber reinforcement. It should be possible to characterize accurately the filler-rubber bond by the two constants F_e, the force needed to break it, and σ, the area per attachment. For poor reinforcing fillers, F_e should be smaller and σ larger than the values found for MPC black. In addition, the temperature variation of σ and F_e may possibly allow one to compute the energy of the rubber-filler bond. The quantity b is a measure of the distance between filler particles. For a given filler size and loading, b should increase as the filler dispersion becomes better.

APPENDIX I

Consider the two filler particles shown in Figure 6. Although it is not necessary to do so, we assume them to be cubical in shape and to be dispersed uniformly through the rubber. Suppose the rubber is stretched so that the centers of the two particles separate a distance ΔL. Using the definition of α, α' and the distances L_0 and L_0' shown in Figure 6, one has

$$-\Delta L = (1 - \alpha) L_0$$

and

$$-\Delta L = (1 - \alpha') L_0'$$

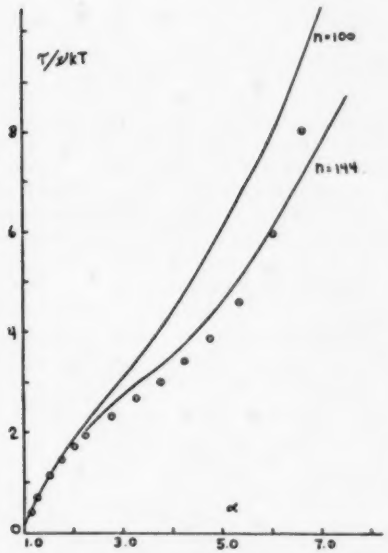

FIG. 6.—Comparison of the experimental stress-strain curve for SBR gum stock (points) with the James-Guth equation.

But since $L_0' = L_0(1 - v_f^{\frac{1}{3}})$, one can equate the expressions for ΔL and cancel out the distance L_0. The resulting equation can be solved for α' to give Equation (5) in the text.

APPENDIX II

Consider two filler particles with radii r. Suppose that their separation may have any value between zero and $2b$ with equal probability. It is desired to find the probability that a point on the surface of one of the spheres is within a distance a of a point on the other sphere. This may be done qualitatively as follows.

The probability that the two spheres are within a distance a of touching is $a/2b$. The surface area of one sphere which is within a distance a of the surface of the other sphere when the spheres are touching is $2\pi ra$. When the spheres have separated to a distance a, none of the area is within a distance a of the other sphere. As an approximation, say that an area πra of one sphere is within a distance a of the other sphere when the sphere separation is a or less. It will be zero when the separation is greater than a.

When any area at all of one sphere is within a distance a of the other sphere, the fraction of the hemispherical ares within a distance a will be $(\pi ra/2\pi r^2)$. This fraction, when multiplied by the probability that the sphere separation is a or less, will give the desired probability. It is $(a^2/4rb]$. If a is taken to be 4 A and b and r to be 150 A this probability is given to be 1.8×10^{-4}.

APPENDIX III

The segment length, a, can be found from a consideration of the stress-strain curve for SBR. Treloar[9] has shown that the James-Guth equation for the

tensile stress is a gum vulcanizate can be written to good approximation as

$$\tau/\nu kT = (\tfrac{1}{3}K)\,[\mathfrak{L}^{-1}(\alpha K) - (3K/\alpha^2)] \qquad (16)$$

with $K = (1/n)^{\frac{1}{2}}$. The quantity n is the number of segments per network chain and ν is the effective number of network chains in unit value.

If one plots Equation (16) in the form $\tau/\nu kT$ vs. α for various values of K, the resultant curves can be compared with actual experimental data plotted in the form $\tau/(\text{const.})$ vs. α. The constant in the experimental plot is chosen so as to fit the theoretical curves at low α values where all the curves must coincide. By comparing the experimental curve with the theoretical curves, one can choose the proper value of K to obtain the best fit. This value of K, in turn, yields a value for the number n of segments per network chain in the rubber upon which measurements were taken. These plots are shown in Figure 7. The experimental data are those of Treloar[9] for SBR gum stock.

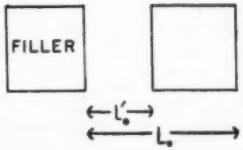

FIG. 7.—A schematic diagram for the computation carried out in Appendix I.

The appropriate value of n appears to be about 140. In addition, νkT, the constant needed for the experimental curve, is about 4.3×10^6 dynes/cm^2. If one assumes that the original gum stock had a number average molecular weight of 35,000, one can then compute the molecular weight of a network chain M_c from the value of ν. This yields a value of about 4800 for M_c. It is therefore known that a chain of this molecular weight contains about 140 segments.

To find a, one makes use of the fact[10] that the mean square end-to-end distance of nearly all common polymers is known experimentally to conform with the relation $R^2 \cong (7.5 \times 10^{-9})^2 M$. Since one also has that $R^2 = na^2$, one can equate these two expressions for R^2 and replace n and M by the values found above. One then finds that a is about 4.3 A.

SYNOPSIS

A molecular theory for the softening of filled rubbers which is caused by prestressing is presented. It is based upon the assumption that the centers of the filler particles are displaced in an affine manner during deformation of the rubber. Those network chains which are fastened at both ends to filler particles will break when the filler particles have separated enough to stretch the chains to near full elongation. The loss of these chains causes a prestressed rubber to exhibit a much lower modulus than did the original rubber. Equations are derived to describe this phenomena and are tested by comparing with data for black filled synthetic rubber. Good agreement is found if the filler surface area per chain attachment is taken as 44 A^2 and if the strength of the chain is 2×10^{-4} dynes. It is shown that the chains break loose from the filler particle

rather than breaking at C—C bonds along the chain. The theory appears to offer a convenient tool for systematic studies of rubber-filler intractions.

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BIAXIAL FATIGUE TESTING OF VULCANIZATES*

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INTRODUCTION

The considerations which aroused our interest in developing a fatigue test for rubber involving a more complex and realistic condition of stressing than the usual flex tests have been discussed in two previous papers[1, 2]. A strain cycle with alternate stretching in two perpendicular directions was selected as being most significant for tire problems. Testing equipment designed and constructed to carry out such fatigue tests has been described and exploratory results included in earlier papers. The present paper gives the results of studies of the fatigue of vulcanizates using this equipment, discusses their significance, and indicates areas of technological usefulness for this type of fatigue testing.

EQUIPMENT AND PROCEDURES

The test machine has already been described[2]. Figure 1 shows the external appearance of the machine; Figure 2 is a view of the four testing stations; and Figure 3 is a photograph of the control unit.

An improvement has been made in the arrangements at the grips. Originally, after the test sheet was clamped in one pair of the grips, necessarily it was grasped at the edges and stretched in order to clamp it in the second pair. At present, when a specimen is mounted, both pairs of grips are clamped at the the circumference of a circle drawn on the unstretched test sheet and one pair of grips can then be pulled back and clamped in the running position. This is much more convenient than the previous arrangement and has resulted in less scattering of the data and in better consistency in the test results with different operators.

Exploratory results have been reported[2] which compare several methods for initiating the failure. In line with these results it has been found to be advantageous in practice to make multiple pinholes in the test sheet rather than a single pinhole. To do this, three needles, .034 in. in diameter, were mounted in the end of a brass rod, 0.25 in. in diameter, at the corners of an equilateral triangle, 0.19 in. on a side. The testpiece is pierced simultaneously by the three needles after it is mounted in the grips. The Micarta ball retainer over the center of the sheet, see Figure 2, serves as a guide for the brass rod during the piercing operation. The use of three pinholes instead of one to initiate the failure not only reduced the mean value of the fatigue life, i.e., the testing time and the standard deviation of the test data but also usually reduced the standard deviation expressed as a per cent of the mean value. This is shown by the results in Table I, secured in a comparison of the two methods for initiating failure in a natural rubber tread compound (Compound B; cure, 30 min. at

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280° F). Twelve testpieces were tested in each case. The ambient temperature was 24° C and the amplitude, 60%.

Examination of the test specimens after failure indicated that the three pinholes did not act cooperatively to accelerate the failure. The failure started at one of the pinholes, the other two remaining practically unenlarged. Thus the reduction in fatigue life by the use of three pinholes apparently comes about by the increased probability of hitting a spot which is more susceptible to crack growth. This may be an indication that there is non-homogeneity in the test sheets on a scale comparable to the size of the pinholes.

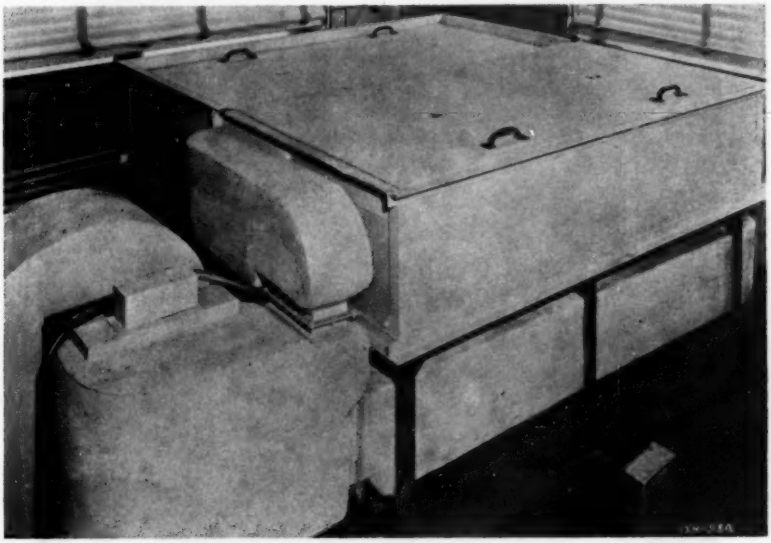

FIG. 1.—Photograph of biaxial flex testing machine.

In comparing the ratings for various elastomers arrived at from the laboratory biaxial fatigue tests with those from service performance it was noted that the laboratory tests rated natural rubber as being much superior to SBR, the spread being far greater than that observed in actual use. It was concluded from this result that our laboratory procedure was placing too much emphasis on tear propagation qualities and too little on crack initiation tendencies in which natural rubber is usually considered to be inferior to SBR.

A system was therefore devised so that initiation of failure by the pinholes was dispensed with and crack initiation occurred during the test due to the controlled exposure of the central area of the testpiece to ozone. The apparatus consisted of a Hanovia No. 2851 quartz lamp which was mounted in a housing with a surrounding glass jacket in a corner of the machine. A small blower created a stream of air between the quartz tube and the jacket. This ozone-bearing stream, by the use of PVC tubing, was made to impinge as a jet on the bottom side of the central area of the testpiece. The ozone concentration could be conveniently reduced by wrapping a portion of the length of the

quartz lamp with aluminum foil. A single station was equipped in this way for the exploratory experiments.

There is usually a considerable rise in the temperature of the testpiece during the biaxial fatigue test. The cycling rate of 680 rpm and amplitudes of 60% or 80% involve an appreciable energy input to the testpiece. The proportion of the energy input which is converted into heat by hysteresis losses in the material becomes a direct factor in the fatigue life through the temperature of the testpiece. It was found, by means of surface temperature measurements with a thermocouple, that raising the ambient temperature from 24° C to 70° C had a much less than proportional effect on the temperature of

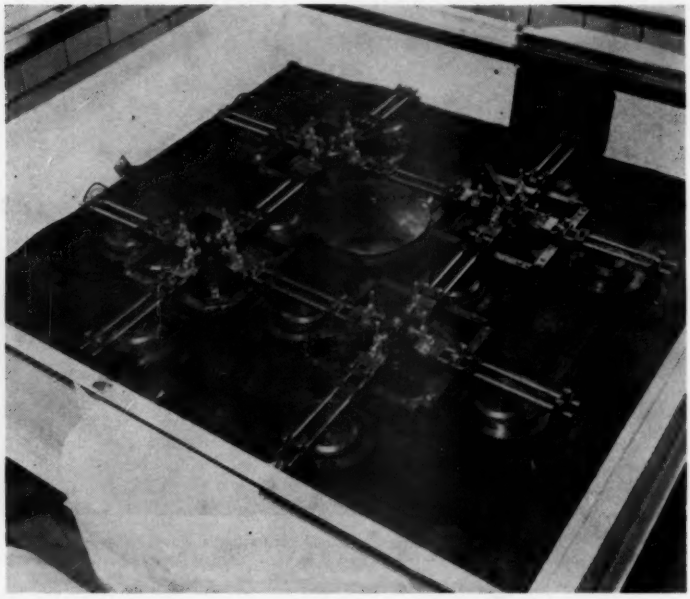

FIG. 2.—Inside view of biaxial flex testing machine.

the testpiece. Evidently, the decrease in hysteresis with increase in ambient temperature in some cases just about offset the increase in ambient temperature as far as the temperature of the testpiece was concerned. A natural rubber tread compound was actually found to have better fatigue life at 70° C ambient temperature than at room temperature and the surface temperature at the center of the testpieces was found to be about 80° C in both cases. The longer flex life at the higher ambient temperature may be due to a more uniform stretching of the testpiece, that is, lower stress concentrations in the central area.

Increasing the ambient temperature evidently has the effect of reducing the effect of hysteresis on the test results. Since the possibility of including the effect of hysteresis to such a marked extent is a rather novel feature of the biaxial fatigue testing technique, most of the tests subsequent to the above observations have been made at an ambient temperature of 24° C so that the

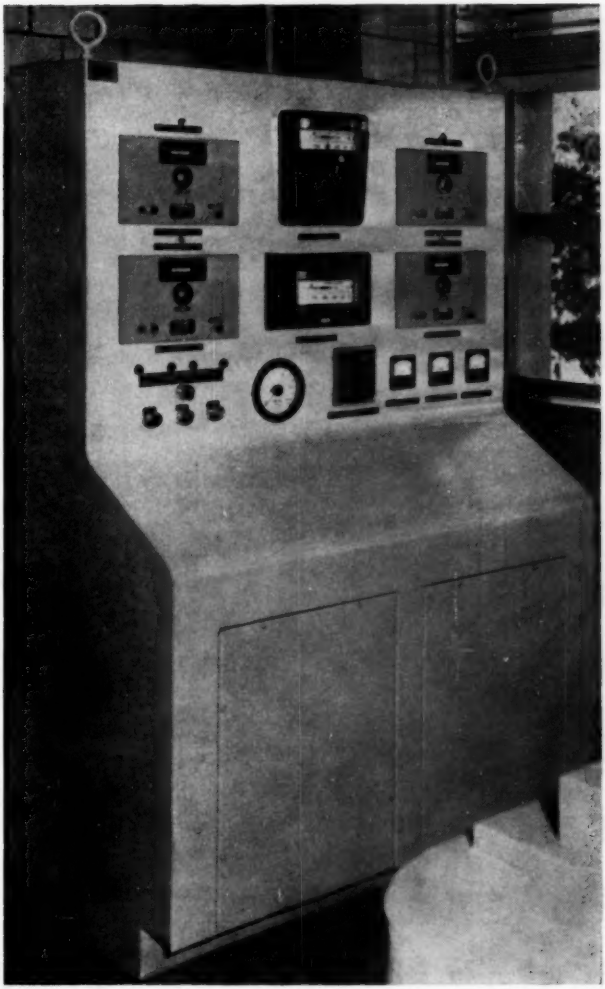

FIG. 3.—Control unit for biaxial flex testing machine.

TABLE I

COMPARISON OF ONE PINHOLE AND THREE PINHOLES FOR INITIATING THE FAILURE

	1 Pinhole	3 Pinholes	% Reduction
Fatigue life (geom. mean), kc	63.5	41.6	34.4
Fatigue life (arith. mean), kc	72.9	45.2	38.0
Standard deviation	38.6	19.6	49.2
% Standard deviation	52.9	43.4	18.0

TABLE II

COMPOUND FORMULAS

	A	B	C	D	E	F	G	H	I	J	K	L	M
Smoked sheet	100	100	100	100	100	100	100	100	100	100			
Cold SBR												100	
Hot SBR											100		
OE SBR													137.5
NBR (67/33)													
Zinc oxide	5	5	5	5	5	5	5	5	5	5	3	3	3
Sulfur	2.75	2.75	2.75	2.75	2.75	2.75	2.75	2.75	2.5	2.5	1.60	1.60	1.50
Stearic acid	2	2	2	2	2	2	2	2	2	2	3	3	2
Mercaptobenzothiazole	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6					
MBTS[1]										0.8	0.45	0.45	0.65
Diphenylguanidine											0.65	0.65	0.90
Di-o-tolyl guanidine										1.2			
Santocure[2]									0.6				
NOBS[3]													
Triethanol amine										0.75			
Phenyl-2-naphthylamine		1	2								1	1	1
Wingstay 100[4]				1	2								
DPPD[5]						0.25	0.50	1					
Regal 300 black													
Regal 600 black													
Regal SRF black													
SRF black													
HAF black	50	50	50	50	50	50	50	50	42				
ISAF black											50	50	68
SAF black													
HiSil 233[6]										45.5			

[1] Mercaptobenzothiazole disulfide.
[2] N-cyclohexyl-2-benzothiazole sulfenamide.
[3] N-oxydiethylene-2-benzothiazole sulfenamide.
[4] Mixed diaryl p-phenylene diamines.
[5] Diphenyl-p-phenylene diamine.
[6] Reinforcing silica.
[7] In the text N-40 indicates a black loading of 40 pts; N-50, 50 pts etc.

TABLE II—(*Continued*)

	N-[7]	O	P-[7]	Q-[7]	R-[7]	S-[7]	T-[7]	U-[7]	V-[7]	W	X	Y
Smoked sheet							100	100	100	100	100	100
Cold SBR		100	100	100	100	100						
Hot SBR												
OE SBR												
NBR (67/33)	100											
Zinc oxide	5	3	5	5	5	5	5	5	5	5	5	5
Sulfur	1.50	2	1.75	1.75	1.75	1.75	2.75	2.75	2.75	2.75	2.75	2.75
Stearic acid	1	3	2	2	2	2	2	2	2	2	2	2
Mercaptobenzothiazole							0.6	0.6	0.6	0.6	0.6	0.6
MBTS[1]	1.5											
Diphenylguanidine			0.25	0.25	0.25	0.25						
Di-o-tolyl guanidine												
Santocure[2]		1.25										
Nobs[3]												
Triethanol amine												
Phenyl-2-naphthylamine	1		1	1	1	1	1	1	1	1	1	1
Wingstay 100[4]												
DPPD[5]		1										
Regal 300 black										50		
Regal 600 black											50	
Regal SRF black												50
SRF black	varied			varied								
HAF black		45	varied				varied					
ISAF black					varied			varied				
SAF black						varied			varied			
Hi Sil 233[6]												

actual temperature of the testpiece depends more upon the hysteresis loss than if the ambient temperature were raised.

The compound recipes are given in Table II.

STATISTICAL CHARACTER OF THE DATA

To study more closely the statistical nature of the data and the effect of various test conditions on the distribution of the results, one hundred testpieces of a cold rubber tread compound vulcanized at the "best" cure were tested under each of the following circumstances:

Ambient temperature	Amplitude	Crack initiation
24° C	60%	1 pinhole
24° C	80%	1 pinhole
70° C	60%	1 pinhole
70° C	80%	1 pinhole

Examination of the results indicated that the distribution of the fatigue-life determinations was markedly skewed. This is shown by the histogram in Figure 4, the appearance of which suggested a lognormal distribution[3]. The approximate applicability of the lognormal distribution is confirmed by the presentation of the results in Figure 5, the abscissa scale being the normal probability scale and the ordinate scale being logarithmic. The one hundred individual fatigue life values in each of the four experiments were ranked in order of magnitude and every fifth value plotted as shown. Three of the test conditions yielded straight line plots with not unreasonable scattering indicating approximate conformance to a lognormal type of distribution. For unknown reasons, the test conditions of 70° C and 60% amplitude gave a plot which is much better fitted by two lines than by one straight line. Figures 6 and 7 give histograms for the data from two of the experiments and show the frequency

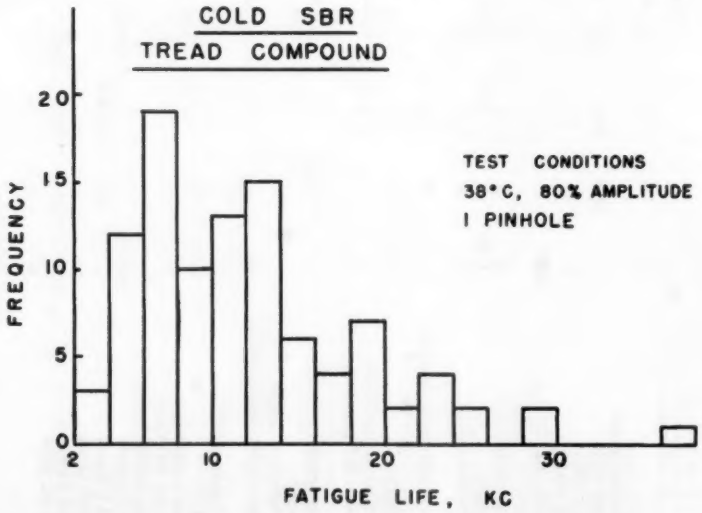

FIG. 4.—Histogram of 100 fatigue life values.

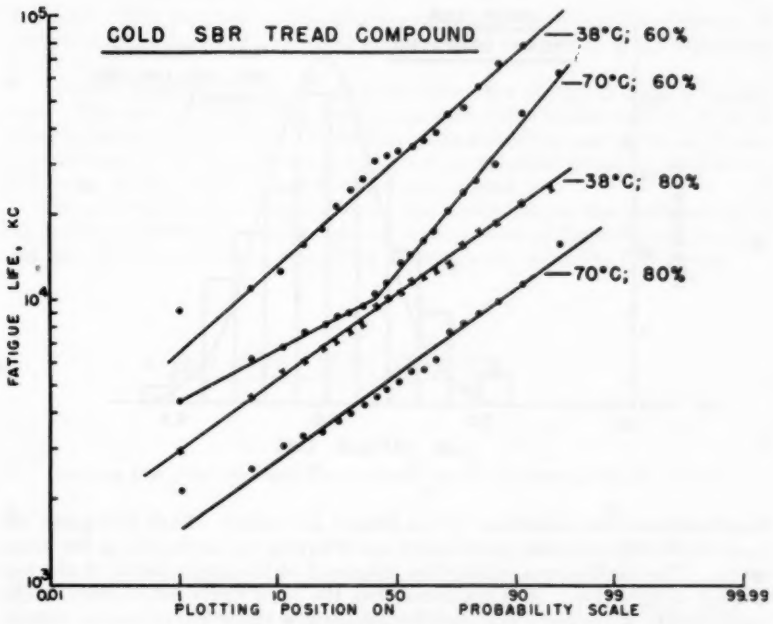

FIG. 5.—Plot of fatigue life data on probability paper.

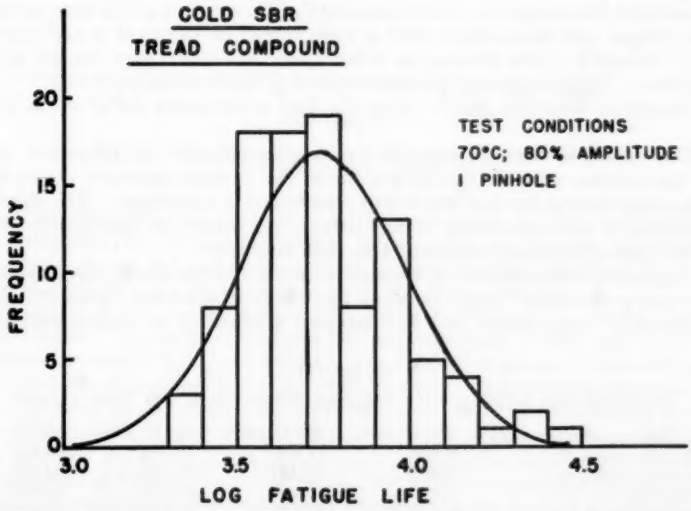

FIG. 6.—Frequency distribution for the logarithm of the fatigue life; 70° C, 80% amplitude.

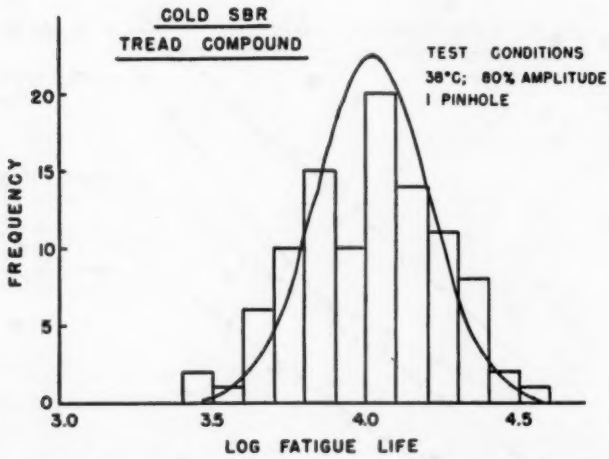

FIG. 7.—Frequency distribution for the logarithm of the fatigue life; 38° C, 80% amplitude.

distribution of the logarithms of the fatigue life values. Each histogram has been fitted with a normal distribution curve having the same area as the histogram. This facilitates a qualitative judgment of the applicability of the lognormal distribution. It is apparent that the fit is fairly satisfactory. The applicability of the lognormal distribution permits statistical principles derived for the normal distribution to be applied provided the logarithm of the fatigue life is used instead of the fatigue life itself. It also lends support to the use of the geometric mean rather than the arithmetic mean of individual test values to characterize the fatigue life of a vulcanizate[2]. To secure a useful average value from fatigue test data which show a wide spread in values it is necessary to avoid distortion of the average by a few specimens which may run for a very long time. This is a general characteristic of all kinds of fatigue tests.

Statistical measures derived from the four experiments are given in Table III.

The extent of the agreement is noteworthy between the geometric mean and the median which is the fatigue life of the average specimen rather than the average fatigue life and which is so convenient to determine. The standard deviations of the logarithms of the fatigue life values are perceptibly larger for the higher ambient temperature at each amplitude.

Figure 8 is a presentation of the results from two of the above experiments on "extreme probability" paper based on the theory of extremal values developed by Gumbel[4, 5] and others and its simplified application to fatigue testing by

TABLE III

STATISTICS FOR FATIGUE LIFE DETERMINATIONS WITH 100 TEST VALUES

Cold SBR tread compound	70° C; 80%	38° C; 80%	70° C; 60%	38° C; 60%
Arithmetic mean, kc	6,809	11,950	20,724	39,915
Geometric mean, kc	5,592	10,437	14,930	32,440
Median, kc	5,100	10,590	13,295	32,935
Mean log	3.74757	4.01857	4.17405	4.51110
Standard deviation (of logs)	.237	.178	.318	.278

Godfrey[6]. This is a more advanced and presumably more significant statistical treatment for fatigue test data than that provided by the use of the lognormal distribution.

To make the plot, the individual test values were ranked in order of magnitude. The abscissa or plotting position for each value is the ratio $m/(N + 1)$ where m is the rank of the particular test value above the lowest one in the experiment and N is the number of tests. As a practical measure, only every fifth value in each series of one hundred was plotted.

The occurrence of a straight line for this plot indicates the applicability of the statistical theory of extreme values. Comparison of Figures 5 and 8 shows that the theory provides a significant improvement over the log normal ap-

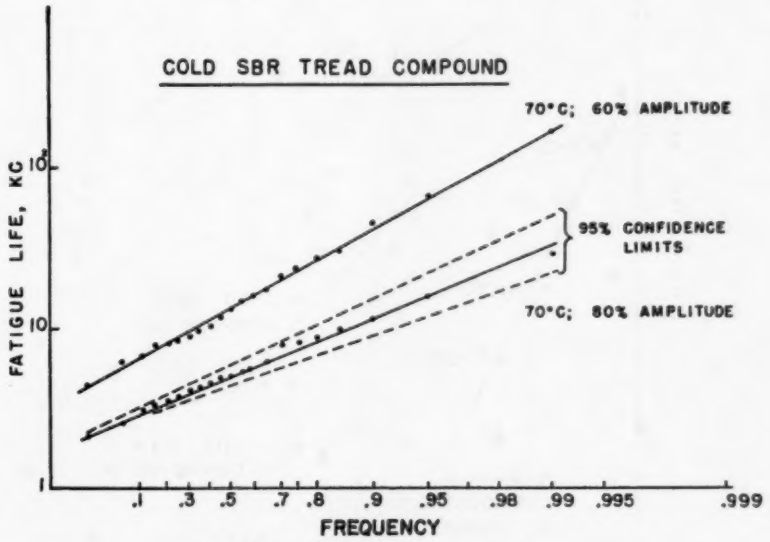

FIG. 8.—Plot of fatigue life data on extreme value probability paper. Every fifth point of the test data is plotted.

proach for describing the distribution of the test values for the runs at 70° C. Unfortunately, the overall advantage is not clear-cut because the highest ranking points for the two runs at 38° C (which are not plotted in Figure 8) fell below the straight line representations for these runs.

In Figure 8, the median fatigue life occurs at the abscissa .500 on the frequency scale. To further illustrate the interpretation of the plot, for tests of this compound at 70° C and 80% amplitude, 75% of the specimens will have failed at 7400 cycles since this is the ordinate corresponding to the frequency of .750. In 95% of the times, this value will not exceed 9200 cycles or be less than 6000 cycles. The confidence limits shown for this run were calculated according to the procedure given by Godfrey[6]. Relatively simple rank-sum tests for determining the significance of fatigue test data are especially advantageous because they do not involve any assumptions about the type of distribution of the test results[7].

COMPARISON OF THE BIAXIAL FATIGUE LIFE OF SEVERAL SBR TYPES

Tests were made with similar compounds of hot, cold, and oil extended SBR to establish the spread which could be expected with the biaxial fatigue test for these polymers with which there has been a wide practical experience in fatigue performance.

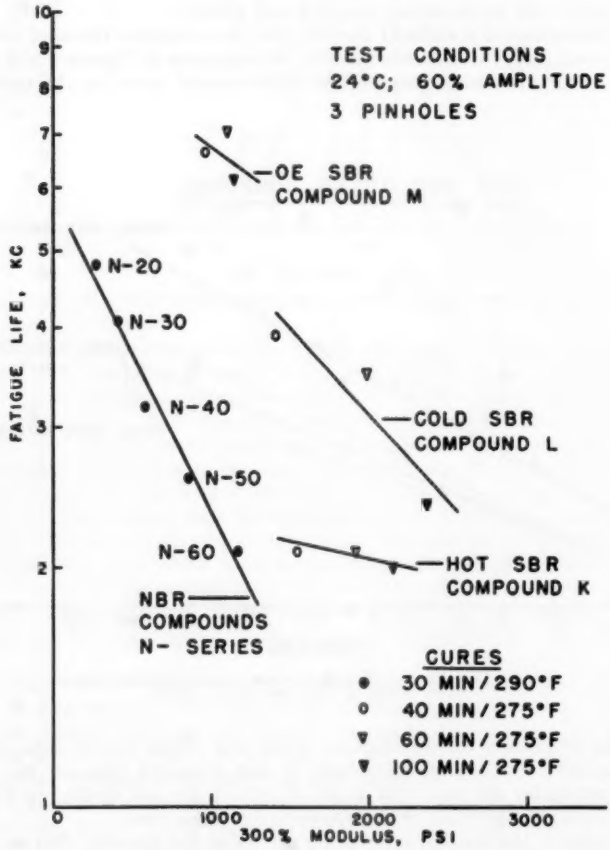

FIG. 9.—Biaxial fatigue life of SBR polymers as a function of modulus.

To secure more generality in the comparison, the results are plotted in Figure 9 as a function of modulus so that the fatigue life can be compared at the same modulus[8]. The relative position of the polymers on the plot is consistent with most experience with these types of SBR. The superiority of OE-SBR in the test does not appear to be due entirely to the lower modulus of the compound.

A plot of the test results with NBR compounds with different loadings of

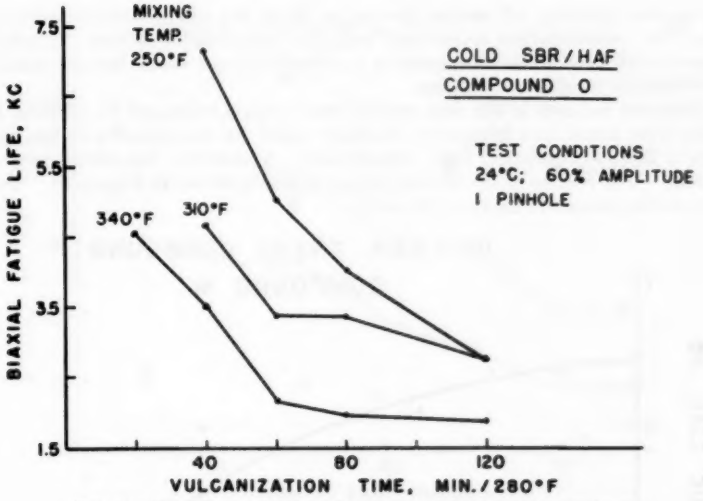

FIG. 10.—Dependence of biaxial fatigue life on mixing temperature and cure with N-cyclohexyl-2-benzothiazyl sulfenamide as accelerator.

SRF black is included in Figure 9 to show the close relationship found between the modulus and fatigue life with the series of black loadings. The results are, of course, not directly comparable with those from the other polymers, the compounds of which contained HAF black.

EFFECT OF PROCESSING VARIABLES

The fatigue endurance of a vulcanizate can be affected by processing variables which determine such factors as the final molecular weight, oxidation products, gel formation and scorching, and the dispersion of the filler, any of which may affect the overall quality of the vulcanizate. A good fatigue test should be reasonably sensitive to any lowering in quality arising from deviations from good processing practices.

The most obvious and general effects of processing variations on quality are exerted through the influence which they have on the dispersion of the filler and on the molecular weight of the rubber. Here the effect of the processing temperature on a vulcanizing system was studied as a simple sample of the effect of a processing variation on the biaxial fatigue life.

It is fairly well known[9] that if a masterbatch containing a sulfenamide type of accelerator is subjected to high mixing temperatures, the accelerator may

TABLE IV

EFFECTS OF MIXING TEMPERATURE
Compound O, Cure: 40 min/280° F

Mixing temperature	100% modulus, psi	Tensile strength, psi	Breaking elong., %	Relative tensile product	Relative fatigue life
250	392	4219	520	100	100
310	386	4626	510	107	65
340	549	4709	410	92	49

decompose, splitting off amine groups, so that the characteristic induction period for vulcanization is reduced and the compound becomes "scorchy". Experiments were made to determine how these effects would become evident in the biaxial fatigue test results.

Different batches of the cold rubber tread type Compound O, without the sulfur, were mixed in a laboratory Banbury mixer for two minutes at temperatures of 250° F, 310°, and 340° respectively. The sulfur was added later on the mill. The results of the biaxial fatigue tests are shown in Figure 10. Each point is the geometric mean of 16 tests.

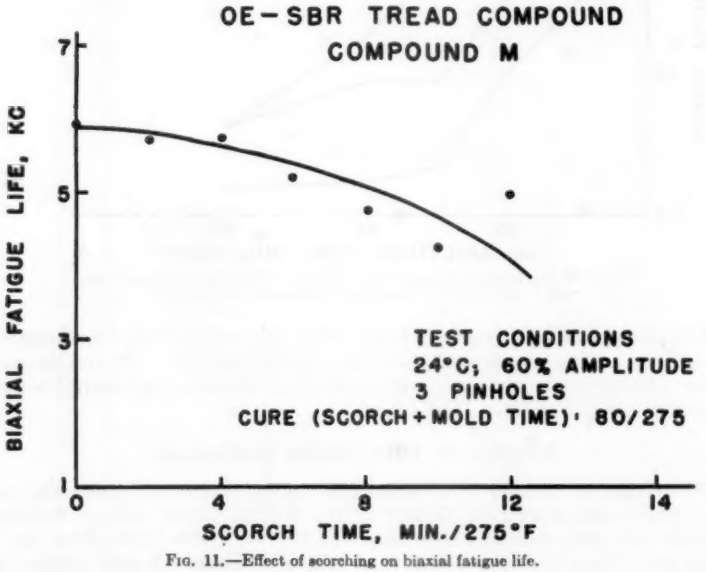

FIG. 11.—Effect of scorching on biaxial fatigue life.

The effect of the mixing temperature was quite pronounced in the fatigue test results. It is apparent from Figure 10 that the principal effect of raising the mixing temperature was to shift the fatigue life vs vulcanization time plot to the left along the time axis, i.e., the higher mixing temperature acted as if it were adding vulcanization time. The increase from 250° F to 340° F in mixing temperature shifted the curve about 50–70 minutes along the vulcanization-time axis. The higher mixing temperature was much more detrimental to the biaxial fatigue life than it was to the stress-strain properties as is shown in Table IV.

Scorching during processing may affect the fatigue life adversely as is indicated by the experimental results shown in Figure 11. In this experiment, the compounded stock was given a scorch or precure by molding it in the form of a block 0.5 in. in thickness and maintaining the temperature at the curing temperature for a definite portion of the total cure time in order to scorch the stock in a controlled way. The block was then transferred to another mold and molded in the form of a sheet 0.79 in. thick and the cure completed at the same temperature. The sum of the scorch time and the time in the sheet mold was held constant.

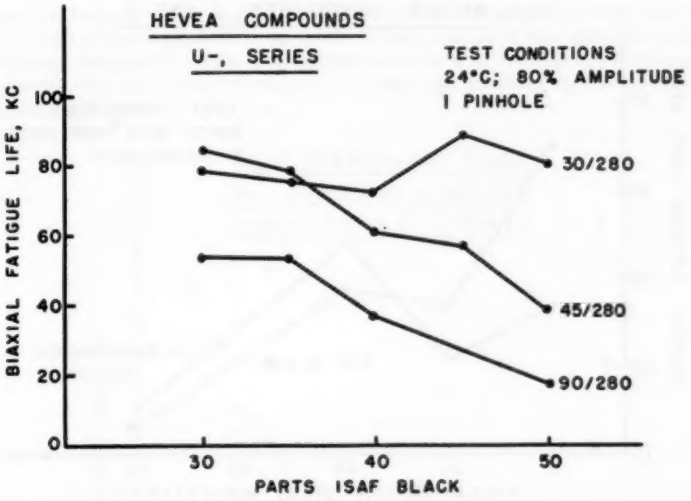

FIG. 12.—Effect of loading of ISAF black and cure on the biaxial fatigue life of natural rubber.

EFFECT OF CARBON BLACK LOADINGS ON BIAXIAL FATIGUE LIFE

Extensive studies were made of the effect on biaxial fatigue life of various loadings of different types of carbon black in natural rubber and in SBR using simple tread type formulations. Each point on the graphs is the value of the geometric mean from 16 tests.

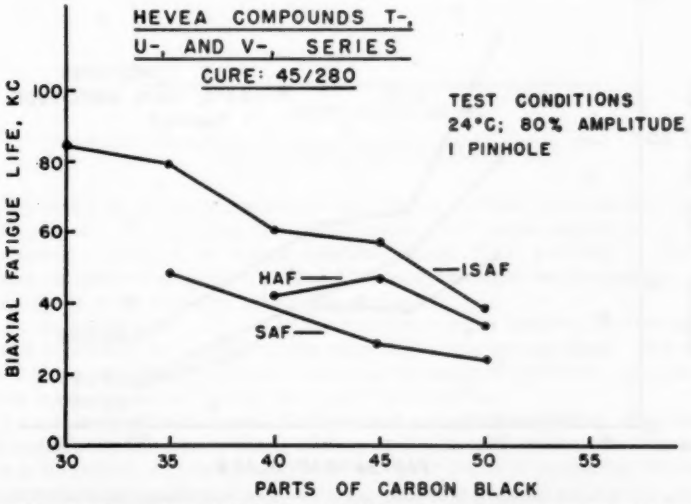

FIG. 13.—Comparison of SAF, ISAF, and HAF carbon black loadings in natural rubber.

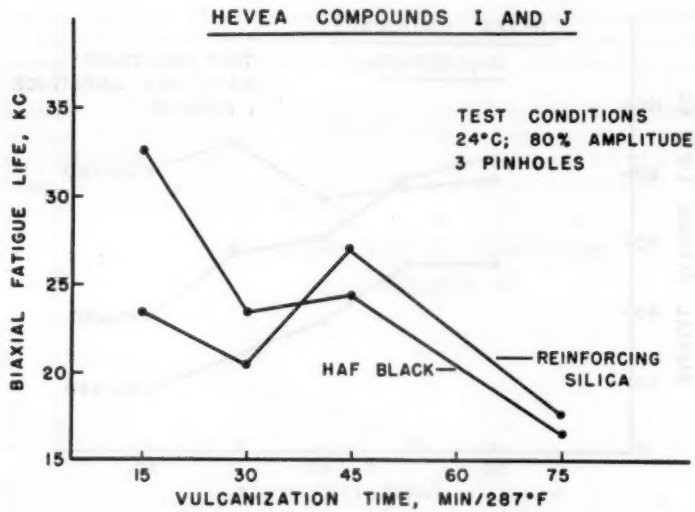

FIG. 14.—Comparison of HAF black and a reinforcing silica.

Figure 12 shows the pattern of the results secured for a range of loadings and of cures with ISAF black in natural rubber. Except at the lowest cure, the fatigue life falls off progessively with increased black loading, i.e. there is no evidence of an optimum loading. The fatigue life also falls off with increased cure. This is especially noteworthy because the modulus, tensile strength, and

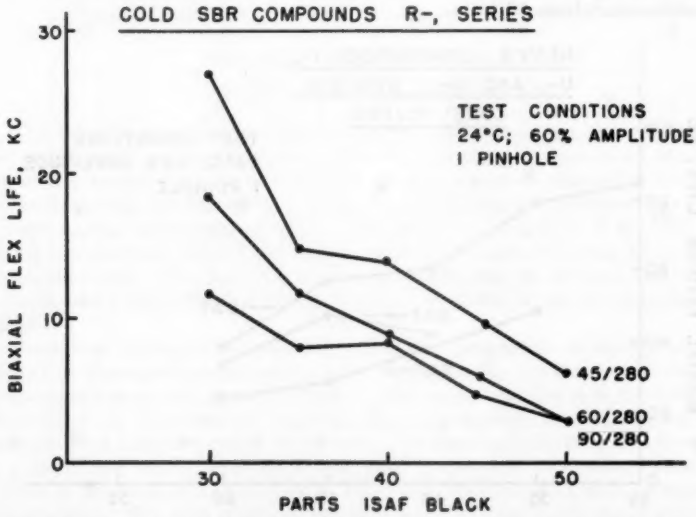

FIG. 15.—Effect of loadings of ISAF black, and of cure on the biaxial fatigue life of cold SBR.

elongation values for the 30 min and 45 min cures indicated that this was a very flat portion of the vulcanization curve. Thus, just as in the previous section, the biaxial fatigue life data emphasizes some sort of deterioration in quality associated with advanced vulcanization which was scarcely apparent from the stress-strain data.

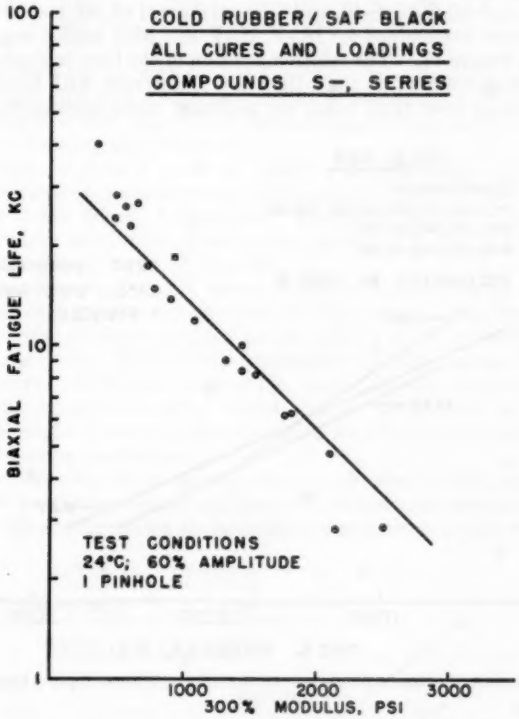

FIG. 16.—Relationship of biaxial fatigue life to modulus for cold rubber compounds with loadings of SAF black.

Figure 13 gives a comparison of the results secured with three types of carbon black. The ranking in order of quality for biaxial endurance of these compounds appears to be rather definitely ISAF, HAF, and SAF. But the differences are not so great but that this ranking might be changed by compounding or, even possibly, processing variations.

As shown in Figure 14, HAF black at lower cures imparted better biaxial fatigue resistance to natural rubber than did a reinforcing silica. But there was little or no difference between them in the range of optimum cures and for higher cures, the silica loading was somewhat superior.

As with natural rubber, cold SBR showed a pronounced falling off of biaxial endurance with increase in black loading and with increase in cure, Figure 15. This is somewhat surprising in view of the poor physical properties of a cold-rubber gum compound.

The biaxial fatigue life of SBR compounds with carbon black loadings exhibited a close connection with the 300% modulus as already observed by Auer, Doak, and Schaffner[8] for cut-growth resistance. In Figure 16 is shown the most probable straight line determined by the method of least squares to represent the points on a plot of log fatigue life vs 300% modulus for all of the cures of the SAF black-loaded SBR compounds which were tested, viz., Compounds S-15, S-20, S-25, S-30, S-35, S-40, and S-50 vulcanized 45, 60, and 90 min/280° F. Similar lines were determined for ISAF, HAF, and SRF loaded compounds and are plotted in Figure 17. The relative position of the lines indicates a deleterious effect of reinforcement on the fatigue life. However, SRF black appears to lose its advantage over HAF black for modulus values greater than 1500 psi.

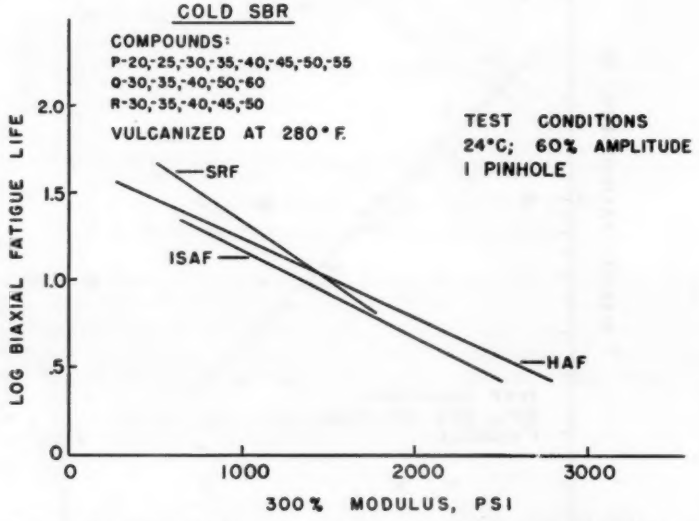

FIG. 17.—Comparison of biaxial fatigue life of cold SBR with different types of black loadings.

The line for SAF black in Figure 16 was not redrawn in Figure 17 because it lies close to and crosses the lines for the HAF and ISAF blacks. Although hysteresis and heat generation play a part in these tests it is dubious that they are the controlling factors in the pattern of results. More probably, reinforcement introduces complex, localized stresses and fibering tendencies which are basically responsible for reduced fatigue life in the biaxial test.

EFFECT OF PROTECTIVE AGENTS ON BIAXIAL FATIGUE LIFE

One of the functions which is desirable for a laboratory fatigue test is to help to determine the relative effectiveness of protective agents such as antioxidants and antiozonants for improving the durability of rubber compounds. Such materials frequently improve the fatigue life of vulcanizates even before any appreciable aging has occurred. More thorough evaluations of the effectiveness of the additives can be obtained by comparing the fatigue life of the vulcanizates after accelerated aging, limited service, or shelf aging. Even

TABLE V

RELATIVE IMPROVEMENT IN PROPERTIES BY ADDITION OF PBNA TO COMPOUND A

Parts PBNA	300% modulus	Tensile strength	Breaking elongation	Tensile product	Biaxial fatigue life
0	100	100	100	100	100
1	106	109	102	110	136
2	103	121	118	131	187

though direct correlations with service conditions may be difficult, the laboratory fatigue tests can give useful indications for screening such materials and for determining how they can best be used and under what conditions they can be expected to be most advantageous.

The addition of 1 or 2 parts of phenyl-2-naphthylamine (PBNA) to a natural rubber tread-type compound, Compound A, resulted in a pronounced improvement in the biaxial fatigue life. There was also an improvement in the tensile strength and breaking elongation, as shown by the relative values in Table V, for the "best" cure, 30 min/280° F.

The comparisons in Table V create some uncertainty as to whether the improved fatigue life is a consequence of the general enhancement of the physical properties of the compound due to PBNA or to protective action of PBNA during the test. Everything considered, the latter alternative appears to be more likely. However, as shown in Figure 18, the improvement in biaxial fatigue life brought about by PBNA was not accentuated by one year of shelf aging, as might reasonably be expected if its effect on the fatigue life was through a protective mechanism.

Figure 19 shows the improvement observed in the biaxial fatigue life of a natural rubber tread-type compound due to the addition of one and of two parts of Wingstay 100 and indicates an interesting dependence on the state of cure.

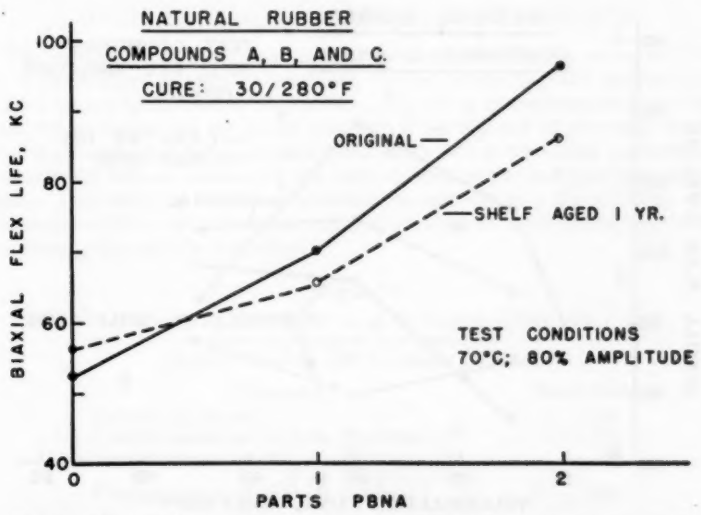

FIG. 18.—Effect of PBNA on biaxial fatigue life of a natural rubber tready-type compound.

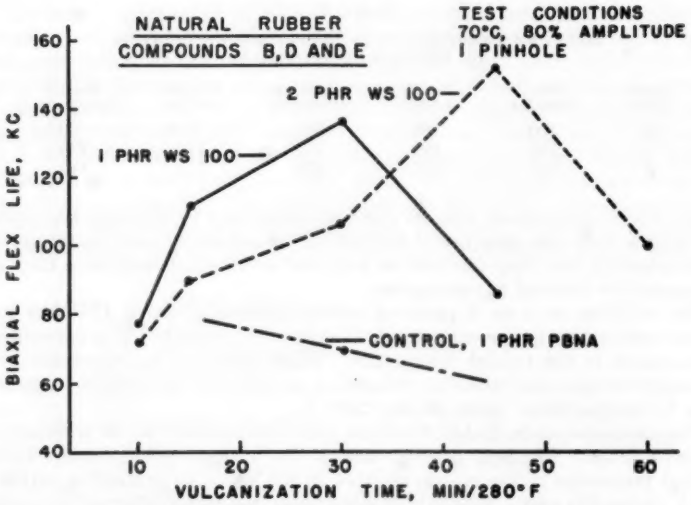

FIG. 19.—Effect of Wingstay 100 on the biaxial fatigue life of a natural rubber tread-type compound.

Each point is the geometric mean from 16 tests. Here, in contrast to the case with PBNA and the situation brought out in Table V, there was practically no change in the physical properties to confuse the issue. The improvement brought about in biaxial fatigue life appears to be due entirely to the protective action of the additive in this case. Figure 20 presents a comparison of the

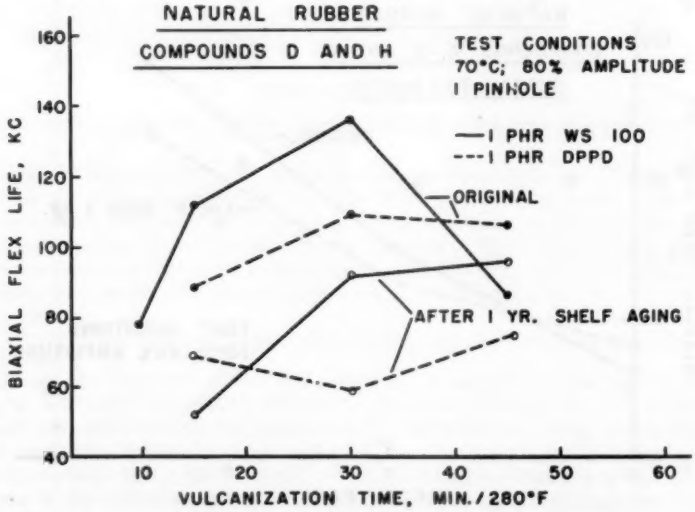

FIG. 20.—Biaxial fatigue life of a natural rubber tread-type compound with 1 phr of Wingstay 100 or of DPPD.

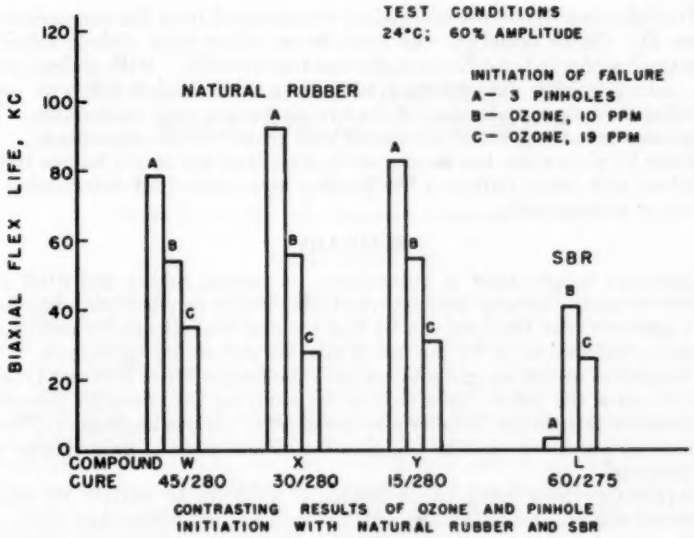

FIG. 21.—Contrasting results of ozone and pinhole initiation with natural rubber and SBR.

original biaxial fatigue life and that after one year of shelf aging with one part of Wingstay 100 or of DPPD in the natural rubber tread-type compound over the range of cures. The changes in physical properties due to shelf aging appeared to be dominated by post-curing rather than by oxidative effects.

OZONE TESTING WITH THE BIAXIAL TECHNIQUE

The conversion of the biaxial fatigue procedure to employ ozone for initiation of the failure, as already described, yielded interesting and instructive results which are illustrated in Figure 21. The ozone concentrations were determined by sampling the air about one inch from the end of the tube through which it emerged and hence corresponded fairly well to the ozone concentration to which the bottom surface of the central area of the test specimen was exposed. They are not, of course, ambient concentrations in the machine. The test results with ozone initiation of the failure showed considerably less scatter than those with pinhole initiation.

TABLE VI

BIAXIAL FATIGUE LIFE OF A NEOPRENE COMPOUND WITH DIFFERENT ANTIOZONANTS
(Amplitude, 80%; 24° C; Ozone initiation)

Antiozonant	Biaxial fatigue life, kc
Control compound —	144
Control compound + 2 pts Wingstay 100[1]	187
Control compound + 5 pts Wingstay 100[1]	276
Control compound + 2 pts Wingstay 100 + 3 pts NiDBDC[2]	305

[1] Mixed diaryl p-phenylene diamines.
[2] Nickel dibutyldithiocarbamate.

The following significant conclusions are apparent from the comparisons in Figure 21. Ozone initiation was much more severe than pinhole initiation for natural rubber but just the opposite was true for SBR. With pinhole initiation, natural rubber outperformed SBR by a wide margin but with ozone initiation the fatigue endurance of the two elastomers were comparable. The latter result is in much better agreement with general service experience.

Table VI gives a few test results which show that the biaxial fatigue testing procedure with ozone initiation has promise as a method for determining the efficacy of antiozonants.

SUMMARY

Extensive fatigue tests of vulcanizates of natural rubber and SBR were carried out using a cycle of alternate stretching in two perpendicular directions.

It is shown that the data can be best handled statistically by assuming a lognormal distribution or by the use of extreme probability techniques.

Illustrative results are given to compare the fatigue life of different types of SBR; to show the value of the method for studying the effects of processing variations on fatigue life; to determine the effect of various loadings of different types of carbon black; and to evaluate the effectiveness of anitoxidants and antiozonants.

Exploratory tests using ozone instead of pinholes to initiate the failure eliminated the wide range in fatigue life between natural rubber and SBR, and in this respect gave a result which is more consistent with general service experience.

This type of biaxial fatigue testing has many areas of usefulness for developing good endurance qualities in vulcanizates.

ACKNOWLEDGMENT

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NON-LINEARITY IN DYNAMIC TESTS. I. VIBRATION TEST METHODS *

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INTRODUCTION

In the analysis of the dynamic behavior of rubber it is usual to assume that the underlying laws are linear. The results of the tests are commonly interpreted by assuming that a second order linear differential equation with constant coefficients adequately describes the motion[1]. This assumption which is made because the relevant mathematical analysis is available, is, however, incorrect and its application may lead to serious errors and misleading conclusions regarding the dynamic stress strain properties of rubber. That the linear, second-order equation with constant coefficients is ,strictly speaking, inapplicable is clear when it is noted that the experimental results show that the coefficients, assumed constant in the mathematical analysis, vary with frequency, amplitude and other experimental conditions.

If the data are to be used solely to determine "effective" values of empirical quantities which have the general character of elasticity and damping which are to be used for engineering applications operating under conditions similar to those of the test then it is probably adequate to accept the linear equation[2].

On the other hand, the results of dynamic tests are extensively used to indicate the character of the molecular structure of rubber. In this important use of dynamic test results the fundamental form of the stress-strain curve must not form part of the mathematical analysis; the data itself must provide the information, not only on the values of the parameters, but also on the functional form of the expressions defining the stress-strain properties[3].

Whereas other authors[4, 5] have drawn attention to limitations which result from the assumption of the functional form of stress-strain curves their subsequent analysis departs from the principle that no assumption should be included in the mathematical apparatus. In References 4 and 5 the stress and strain are assumed to be related in that a polynomial function of partial differentials of stress with respect to time equals another polynomial function of partial differentials of strain also with respect to time. The coefficients of the polynomials are assumed to be constants. It is also assumed that both the stress and strain are simple harmonic. Consideration of these several assumptions in the light of the points made later will show that they are not in keeping with the principle stated. For example, if the material properties are non-linear then it is not possible for both stress and strain to vary in a simple harmonic manner.

Consideration of the problem of the determination of the true dynamic stress-strain behavior must involve either:

(A) Application of a known motion (displacement and velocity) and the measurement of the resulting viscoelastic reaction.

* Reprinted from the *Transactions of the Institution of The Rubber Industry*, Vol. 36, pages 91–122 (1960).

(B) Application of a known cyclic force or of any varying force whose values are known as a function of (say) time, and the recording of the resulting motion in such a form that it can be analyzed without the assumption of a functional form of stress-strain relationship.

Other alternative approaches involve an inbuilt assumption relating the quantities being investigated.

Method A is the basis of the Davies machine[6, 7, 8].

Method B is the subject of the present paper and it will be shown that phase plane methods provide the basis of a method of solution of the motion of a mass on an (unknown) non-linear system.

CONSEQUENCES OF CHOICE OF FUNCTIONAL FORM OF EQUATION

Before proceeding to a discussion of the phase plane method consider the consequences of pre-selection of a governing second order differential equation.

As soon as the experimenter selects one of the available equations he has fixed the functional form of the stress-strain relation and from then on all that can be done is to adjust the numerical values of the parameters to get some kind of "fit".

The fact that the values of the appropriate parameters are determined by experimental measurements of displacement also has important consequences. It is implicitly assumed that the fit to the equation of motion is equally good as the fit to the displacement; this is not so. The equation of motion (such as a second-order linear differential equation) is an equation of forces and involves first and second differentials of the displacements.

To solve this equation, displacement is stated as a function of time. Then the first and second differentials of the displacement function are written down and added in proportions appropriate to the mass, elastic and damping constants to produce an equation like the equation of forces. When the constants in this equation are such that the equation appears to be satisfied at all points in its motion, i.e. at all values of time, the equation is said to be solved and the solution is said to be given by the displacement—time relationship which was originally chosen to do this. Displacement or some characteristics of the displacement such as its amplitude and its periodic time are measured. If a more complex equation than a linear is being fitted other parameters are also determined but basically a displacement whose functional form is assumed is measured and it is mathematically differentiated to deduce the stress-strain characteristics of the material.

Experience in other fields of work[9] led the present author to distrust the assumption that if a function fits the displacement-time curve, the second differential fits the actual acceleration-time curve. Consider a Fourier expansion. The first differential of an nth harmonic has the term n times as important as the corresponding term in the original function. The nth harmonic in the second differential is n^2 as important. Small errors of fit of the displacement function can have an overriding effect on the second differential terms. That there is a reasonable fit between assumed and experimentally determined displacement time curves may mean and in the use of rubber does mean, an extremely poor fit to the force-time curve.

The correct choice of functional form is also important. In the first instance it is important to note that the use of a few terms of either polynomial or

Fourier series does not automatically lead to a true physical interpretation of the phenomena. The following examples will illustrate this point.

Measurements of deflection under twelve or fifteen different loads at each of three places on each of four solid tires of each of twenty-seven different sizes were statistically analyzed. The changes of deflection due to load were fitted by orthogonal polynomials and it was desired to know at which term the polynomial expression should be truncated. In fourteen of the cases the residual variance after the cubic term was not significant and thirteen cases it was significant in relation to the error variance calculated from the tire to tire, within tire and test observation error variances. The equation adopted therefore was cubic but it was not a good fit by common sense as the resulting curve had an undulation not present in the original curves which proceeded smoothly with a

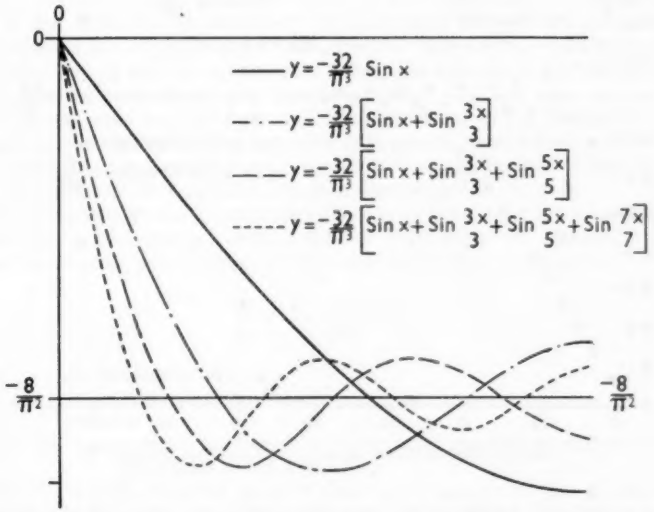


FIG. 1.—Fourier series approximations to second derivative of parabola.

monotonically changing gradient from the origin to be asymptotic to a straight inclined line not through the origin. The inclusion of a quartic term was no solution; it merely introduced one more undulation and, in a number of the cases, increased the residual error. The fault was the fundamental one of using the wrong functional form; a fault which was not rectified by the use of the most refined methods of curve fitting nor by the use of some four thousand results in the analysis.

Another example regarding the effect of functional form is as follows. Manley shows[10] that a good approximation to a sine wave between O and π is given by the parabolic equation

$$y = 1 - \frac{4}{\pi^2}\left(x - \frac{\pi}{2}\right)^2$$

and that the Fourier series corresponding to this equation is

$$z = \frac{32}{\pi^3}\left(\sin x + \frac{\sin 3x}{27} + \frac{\sin 5x}{125} + \frac{\sin 7x}{343} + \right)$$

the amplitude of the second term is one twenty-seventh of the fundamental. This feature that the second term is one twenty-seventh of the fundamental is often taken as indicating that only the fundamental term need be considered, i.e. the parabolic wave form can be replaced by a sine wave. This would lead to the deduction that the velocity is a cosine which is the first differential of a sine. The second differential which is the acceleration, is a minus sine.

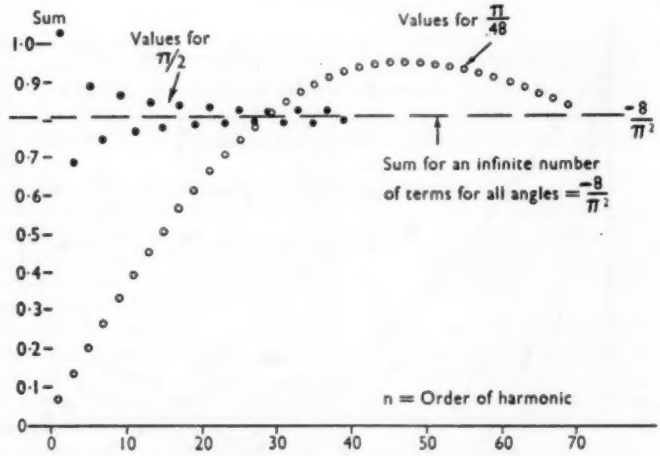


FIG. 2.—Sum of Fourier series for various number of terms.

The functional forms of the velocity and acceleration of the parabolic equation of displacement are, respectively, a straight line and a constant which are very different from the cosine, and sine deduced from the sine approximation to the parabola.

None of this challenges Fourier analysis in its theoretical form but only the rejection of the higher terms before differentiation.

A detailed examination shows that the agreement between a single term approximation and the original parabola is within 5 per cent and a two-term approximation is excellent, the discrepancy being so small that it could not be detected in a diagram drawn in this journal. The discrepancies between the second differentials of the parabolic function and a Fourier series of several terms are however substantial (Figures 1 and 2). Furthermore, the functional form given by the series is not indicative of the correct functional form unless a large number of terms are included.

The above examples establish that it is not adequate to assume an equation of motion and to determine viscoelastic constants from the values of the frequency and amplitude on the basis of that assumed equation.

PHASE PLANE METHODS

Phase plane methods in which no assumptions as to the form of the stress strain relationship are introduced by the analysis can be devised.

Phase plane methods in which motion is described by a trajectory on the phase plane of velocity against displacement, have been used for the solution of specific non-linear equations, such as Van der Pols' relaxation equation[11–16] and linear equations[17]. Any closed loop on the phase plane corresponds to a periodic oscillation; if the viscoelastic system is dissipative then all closed loop trajectories are associated with a cyclic, periodic or recurrent driving force to supply the energy for these losses. Free oscillations of damped systems spiral inwards to the origin of the phase plane.

Trajectories which are circles concentric to the phase plane origin and ellipses whose centers are at the origin, correspond to simple harmonic motion, the circle corresponding to a specific choice of scale determined by the periodic time. If the oscillation is non-linear the trajectory cannot be made a circle concentric with the origin by any choice of scale. For a fuller discussion of the phase plane theory and its application to specific equations the reader is referred to the publications already mentioned[11–17].

The general case has, however, not been discussed in the literature; brief disclosure of the method of dealing with this general case which is free from inbuilt assumption was made in an informal talk to the Bureau of Standards[3], U.S.A., in 1955, and in a contribution to a discussion[17].

It can be shown from first principles (Newton's laws) that in any non-linear or linear spring and dashpot system the law connecting the external driving force and the spring and dashpot reaction can be written in the form:

$$\frac{d\dot{y}}{dy} = \frac{G - f(y, \dot{y})}{m\dot{y}} \tag{1}$$

where y = displacement
$\dot{y}$ = velocity of displacement
m = mass
$f(y, \dot{y})$ = instantaneous values of viscoelastic reaction of system at displacement y and velocity $\dot{y}$
G = instantaneous value of external driving force (see Figure 3).

This equation follows from the mathematical fact that

$$\frac{d^2y}{dt^2} = \frac{d}{dt}\frac{(dy)}{(dt)} = \frac{d}{dt}(\dot{y}) = \frac{d\dot{y}}{dy}\frac{dy}{dt} = \dot{y}\frac{d\dot{y}}{dy}$$

and the physical fact that in a system such as in Figure 3:

mass × acceleration equals external driving force minus spring and dashpot reaction

or

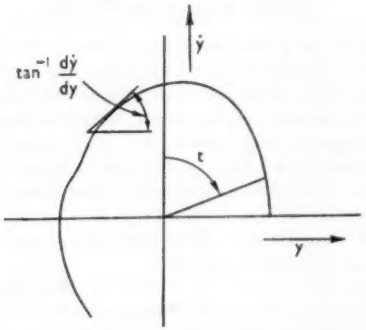
$$m\ddot{y} = G - f(y\dot{y})$$

These relations are always true at all instants of the motion.

Equation (1) can be stated in words as:

Gradient on the phase plane diagram at any point equals

$$\frac{\text{External driving force—viscoelastic reaction}}{\text{momentum}} \tag{2}$$



$$\frac{d\dot{y}}{dy} = \frac{\text{External driving force} - \text{Viscoelastic Reaction}}{\text{Momentum}}$$

FIG. 3.—Gradient of phase plane trajectory.

The trajectory on the phase plane, as the curve relating $\dot{y}$ and y is called, describes precisely the motion of the oscillating mass and Equations (1) or (2) show how this curve (or more specifically its gradient) is related to the viscoelastic reaction and applied external force. The viscoelastic reaction is dependent on the properties of the rubber in the case in which we are interested.

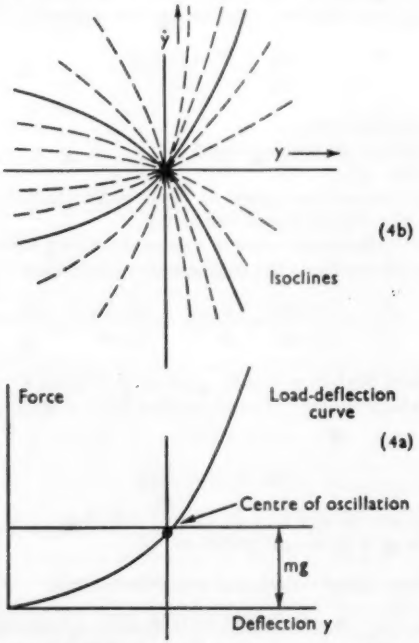


FIG. 4.—Relation between isoclines and load—deflection curve when there is no damping.

Case of rubber in compression without damping.—Before proceeding to the specific case which is one of non-linear elasticity without damping and without external driving force, it would perhaps be stated in any such case the isoclines or lines joining points of equal gradient on the phase place are merely the elastic stress-strain curve drawn at various scales (Figure 4).

For if $G = 0$

$$m\dot{y}\frac{d\dot{y}}{dy} = f(y, \dot{y}) = g(y)$$

where g is used for the functional form to avoid confusion with the general case.
i.e. $H\dot{y} = g(y)$
where

$$H = m\frac{d\dot{y}}{dy}$$

Hence for any chosen value of $\frac{d\dot{y}}{dy}$, the equation of the isocline (subject to the condition that $g(y) = O$ correspond to the position of rest of the mass, i.e. $\dot{y} = o$) is proportional to the equation of the force due to deflection away from the position of rest. The scale ratio is dependent on the gradient to which the isocline corresponds and the mass.

In Reference 18 an expression for the stress-strain curve of rubber in compression is given as

$$L = \frac{AE\Delta}{(1 - \Delta)^{1.18}} \tag{4}$$

when A = original area
Δ = compression in terms of original height
E = modulus

This is a curve somewhat as in Figure 4*a* and is markedly non-linear. If the mass is put on the spring and subject to the action of gravity it will occupy a position of rest where $f(y) = mg$. From Equation (3) the plot of isoclines in Figure 4*b* can be obtained.

If a series of trajectories corresponding to free oscillations of different amplitudes are drawn a series of curves as in Figure 5 are obtained.

The periodic time of the oscillation can be obtained by a graphical process as shown in Figure 6 because $\dot{y} = \frac{dy}{dt}$ then $\frac{dt}{dy} = \frac{1}{\dot{y}}$. By taking the $\dot{y}$ corresponding to A as the average value operating over the interval of displacement δy which, in time, corresponds to the portion BC of the trajectory we have $DE = k\dot{y}$ where k is a scale factor and so

$$\tan EOF = \frac{OE}{DE} = \frac{P}{k\dot{y}} \text{ where } P \text{ is a constant polar distance} = \frac{N}{\dot{y}} \text{ say.}$$

If GH is drawn parallel to OF then

$$\frac{HJ}{GJ} = \tan EOF = \frac{N}{\dot{y}} = N\frac{dt}{dy}$$

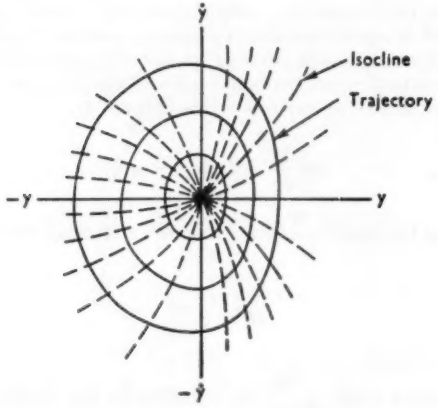


FIG. 5.—Trajectories in the phase plane.

But

$GJ = Q\delta y =$ where Q is a scale factor

$\therefore HJ = QN\delta t = R\delta t$ where R is a constant

If this done step-by-step the full cycle of oscillation can be drawn and the periodic time determined.

For the specific Equation (4) this has been done for several amplitudes and the results are as follows:

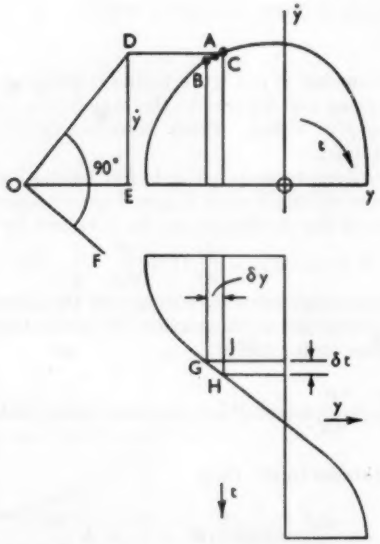


FIG. 6.—Derivation of y—t curve from ẏ—y trajectory.

(1) The periodic time of oscillation is such that if a stiffness were calculated from it by the usual SHM formula the slope of the equivalent linear system would be 7 per cent steeper than the tangent to the curve at the point of static equilibrium.
(2) The periodic time does not change with amplitude.
(3) The oscillation is strictly non-linear.
(4) If an SHM were fitted to the y-t curve derived as in Figure 4 the center of oscillation would appear to have shifted off the elastic curve just as if the material had stiffened. (This is similar to the rectification effect in a wireless valve.)

(*Note* that Figures 4, 5 and 6 are not to scale for the equation under discussion.)

(5) Twenty-four term Fourier analysis of the y-t and $\dot{y}$-t curves derived in this manner gave the following values:

	Displacement curve, %	Velocity curve, %
Constant term	17.7	—
Fundamental	100	100
Second harmonic	6.1	12.1
Third harmonic	0.76	2.27

These values are self consistent, indicating that the analysis was reasonably executed: the high order terms were not self consistent and are not included here as it was concluded that their values were not statistically significant due to their dependence on high order differences and consequent low precision of calculation.

From the above it can be deduced that an acceleration time curve would have a 24 per cent second harmonic and a 6 or 7 per cent 3rd harmonic with also some undetermined higher harmonics.

The presence of a second harmonic in the force-time curve determined by a piezo-electric crystal on a Roelig machine has been experimentally established by Payne[19], but the consequences under discussion here were not mentioned in his paper.

Today it is not usual to employ Equation (4) for rubber in compression (it was used as it was the one available when the analysis was carried out in 1946).

Because of its relation to the James and Guth expression for extension, the expression originally discussed by Jenkins and Cooper[20] for cylinders with lubricated ends, is now more commonly employed[21].

Equation (4) is for tall cylinders[18] and these are equivalent to lubricated ends as most of the cylinder is under pure compression (see Appendix 1 of Reference 18). If the numerical values for the two equations are compared it is found that they are within 2 per cent over the range for which Equation (4) applies, i.e. below 50 per cent deflection. In making this comparison there is the assumption that G, the shear modulus[20, 21] is one third E the compression modulus used in Reference 18. This is true if the volume is constant.

This illustrates that although the analytic form of the solution may look vastly different in the two cases, the graphical solution would be similar as should be the case for the problem is the same physical one and either or both of these expressions are justified solely because they empirically fit experimental values.

The above analysis shows that the common interpretation which ascribes the apparent stiffening (as judged from the application of SHM formula) as being due to a physical phenomena is open to serious doubt and in a number of cases, at least, fallacious. Apparent stiffening judged by the use of linear analysis on non-linear phenomena must be examined and understood mathematically before giving physical names to the phenomena.

It may be thought that mathematicians have proved rigorously that as the amplitude tends to zero so the motion tends to SHM and the frequency to that expected from the slope of the tangent of the curve. This is so in the case in which the Fourier analysis of the stress-strain curve contains only odd harmonics, but it is untrue when the curve contains even harmonics.

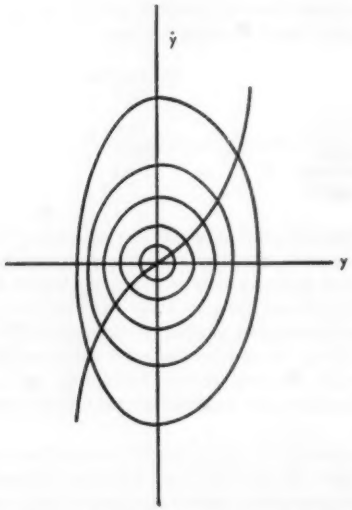


FIG. 7.—A point of inflection at the origin causes small amplitude oscillations to become simple harmonic.

The reason why the oscillation converges to SHM of frequency corresponding to the tangent in the case of a curve with odd harmonics only, is that such curves have a point of inflection at the equilibrium (and the curve is therefore a straight line) and the trajectories become more and more elliptical and hence symmetric around the velocity axis. Ellipses centered about the phase plane origin (which are circles at an appropriate choice of scale) correspond to SHM (Figure 7).

The conclusion is clear. If the stress-strain curve includes a second and other even order terms the oscillation will contain second order and even harmonics and in consequence the calculation of a stiffness from an observed frequency using ordinary linear theory will produce a value which differs from the gradient of the stress-strain curve. The oscillation will also appear to be centered about a point not on the stress-strain curve. These are mathematical facts and are not due to a change in the material's physical properties under dynamic test conditions.

THE GENERAL CASE

Although the above example is a specific case it shows the power of the new approach and some of the consequences of an arbitrary assumption of a mathematical form for the governing equation.

It will now be shown that given two of the following three the remaining one can be found in any given case:

External driving force,
Motion,
Viscoelastic reaction (VER).

This can be done even in cases where the viscoelastic properties do not obey the law of superposition.

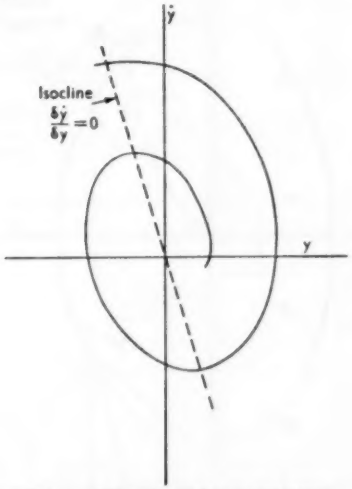


FIG. 8.—Effect of damping on trajectory.

To determine the external driving force to maintain a specified motion for any viscoelastic system.—If the system has damping then under no driving force the trajectories spiral to the origin and the isoclines are such that the isocline for $\frac{d\dot{y}}{dy} = O$ does not lie along the $y = O$ axis (Figure 8).

Consider the case where the trajectory (or better still a family of trajectories) are known for the case of zero driving force. These trajectories are dependent solely on the viscoelastic properties of the material and correspond to:

$$\frac{d\dot{y}}{dy} = \frac{-VER}{m\dot{y}} = \frac{(d\dot{y})}{(dy)_0} \tag{5}$$

Then if a system of isoclines of values $\frac{(d\dot{y})}{(dy)_0}$, corresponding to the required motion is superposed upon the trajectory (or family of trajectories) then at the points of intersection of the $\frac{(d\dot{y})}{(dy)_0}$, isoclines and the trajectories $\frac{(d\dot{y})}{(dy)_1}$, values of

driving force can be determined from:

$$\text{External driving force} = M\dot{y}\left(\frac{(d\dot{y})}{(dy)_1} - \frac{(d\dot{y})}{(dy)_0}\right) \tag{6}$$

If now a closed loop corresponding to a required cyclic motion is drawn in using the motion isoclines $\frac{(d\dot{y})}{(dy)}$, the values of external driving force can be entered on it by graphical interpolation from the surrounding values of the two sets of $d\dot{y}/dy$.

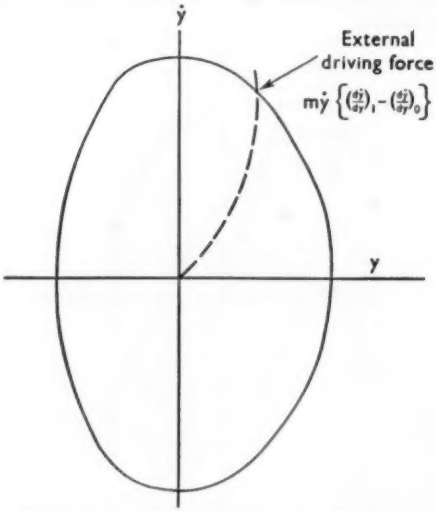


FIG. 9.—Derivation of driving force to obtain a given motion for system with known viscoelastic properties.

Alternatively, if the closed loop trajectory corresponding to the required motion and the isoclines corresponding to the viscoelastic system are known in the first instance then values of external driving force can be written at the intersection points in a similar manner, but in this case without interpolation (Figure 9).

If isoclines for both motion and viscoelastic system are known the former can be used for the determination of a motion trajectory and the previous process applied or, as an alternative, the differences between isocline values at any point can be used to calculate the driving force.

In all cases the time interval corresponding to the motion between any two adjacent points on the trajectory can be obtained from $dt = \frac{dy}{\dot{y}}$ and summed

as required to obtain the driving force-time curve or by the construction of Figure 6.

Hence given the viscoelastic reaction in terms of the displacement and velocity, and an impressed motion, the driving force to maintain that motion can always be obtained. This is true even when the law of superposition does not hold, e.g. the damping coefficient is not the same at all deflections.

This problem could also be dealt with by the graphical procedure now to be described to solve the reverse problem, that is, given the external driving force and viscoelastic properties, find the motion.

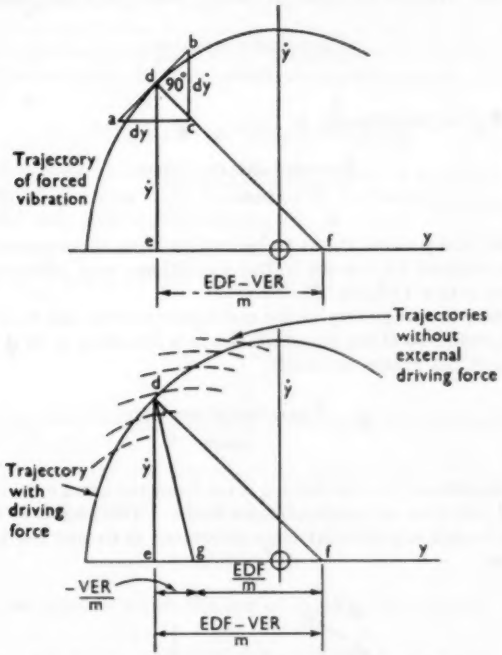


FIG. 10.—Relation between external driving force (EDF) and viscoelastic reaction (VER) and subnormals.

To find the motion given the viscoelastic properties and the external driving force.—As a preliminary it should be noted from Figure 10*a* that at any given point on the trajectory representing the motion of a non-linear system, the subnormal to the trajectory at a given point is proportional to the ratio

$$\frac{\text{External driving force minus viscoelastic reaction}}{\text{mass}}.$$

This follows from

$$\dot{y}\,\frac{d\dot{y}}{dy} = \frac{\text{External driving force minus viscoelastic reaction}}{\text{mass}} \qquad (7)$$

and in Figure 10*a*

$$\frac{bc}{ac} = \frac{d\dot{y}}{dy}, \frac{bc}{ac} = \frac{ef}{de} \quad \text{and} \quad de = \dot{y}$$

$\therefore$ the sub-normal

$$ef = de\,\frac{bc}{ac} = \dot{y}\,\frac{d\dot{y}}{dy} \tag{8}$$

Again in Figure 10*b* the segment of the abscissae *eg* which is the sub-normal to the trajectory without an external driving force is proportional to

$$\frac{\text{Viscoelastic reaction}}{\text{mass}}$$

It follows that *gf* is proportional to

$$\frac{\text{External driving force}}{\text{mass}}$$

Assume that the process about to be outlined has commenced from a given starting point defined by known initial conditions, and proceeded along the trajectory from *h* to *d* (Figure 11).

At the point *d* the trajectory of the non-linear system due to the viscoelastic reaction alone would be along *jk*, which lies in a direction so that the normal *dl* to *jk* would meet the *y* axes at *l* and

$$el = \frac{\text{Viscoelastic reaction}}{\text{mass}} \tag{9}$$

Mark off *ln* proportional to the driving force from the known driving force time curve, join *nd* and draw *dp* perpendicular to *dn*. The length of the element *p* can be chosen to suit a particular time increment *dt* to suit the known driving force-time data.

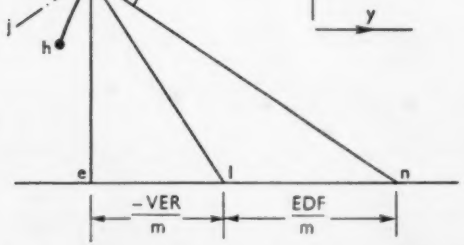


FIG. 11.—Construction to plot trajectory for known viscoelastic properties and external driving force.

To obtain viscoelastic reaction to obtain a given motion with a given external driving force.—This problem is that of finding values of

$$\frac{(d\dot{y})}{(dy)_0} = \frac{(dy)}{(dy)_1} - \frac{EDF}{m\dot{y}} \tag{10}$$

and in principle can be done if the required motion defined by values of $\frac{(d\dot{y})}{(dy)_1}$ and values of the external driving force are known.

The determination is simplest if both the trajectories and the corresponding isoclines for the motion are to hand. Exact details need not be discussed as they can be developed from the earlier cases. It should be noted that the solution to the problem as defined may be unobtainable in practice as the corresponding physical system to the viscoelastic reaction system deduced may not be achievable.

THE LAW OF SUPERPOSITION

The law of superposition is so frequently taken as a primary assumption that it is worth while giving special attention to its consequences.

Consider the case with no driving force

The value of $\frac{d\dot{y}}{dy}$ has a specific value (say) α

when

$$\alpha = \frac{-f(y, \dot{y})}{m\dot{y}} \tag{11}$$

This is an implicit function defining the isocline corresponding to $\frac{d\dot{y}}{dy} = \alpha$. That is, the points satisfying the equation have a value $\frac{d\dot{y}}{dy} = \alpha$. It will be more convenient if we rewrite Equation (11) as

$$m\alpha\dot{y} = -f(y, \dot{y}) \tag{12}$$

Now in those cases in which the law of superposition holds

$$f(y, \dot{y}) = g(y) + h(\dot{y}) \tag{13}$$

where g and h are functions and $f(y, \dot{y})$ is comprised solely of two terms independent of each other. This is obviously a special case of physical behavior although commonly accepted as the general case.

Consider the case of Equation (12) where $f(y, \dot{y})$ is replaced by

$$g(y) + h(\dot{y})$$

i.e.

$$-g(y) - h(\dot{y}) = m\alpha\dot{y}$$

or

$$-g(y) = m\alpha\dot{y} + h(\dot{y}) \tag{14}$$

It is the fact that the law of superposition applies in these cases which enables functions of y to be separated from functions of $\dot{y}$.

As can be seen from Figure 12 and Equation (14) in those cases where superposition applies the points on the isocline of value are those where the values of $-g(y)$ and $m\alpha\dot{y} + h(\dot{y})$ are equal. Furthermore, changes in the functional form of $g(y)$ has no effect on the values along the $\dot{y}$ axis.

As can be seen from Figure 12*b* these relationships enable isoclines for specific values of α to be drawn given $h(\dot{y})$ and $g(y)$. The isocline for a given α can be obtained by using dividers set at distance AB to discover point E on the isocline, by finding point C where $CD = AB$. Care with regard to signs is required.

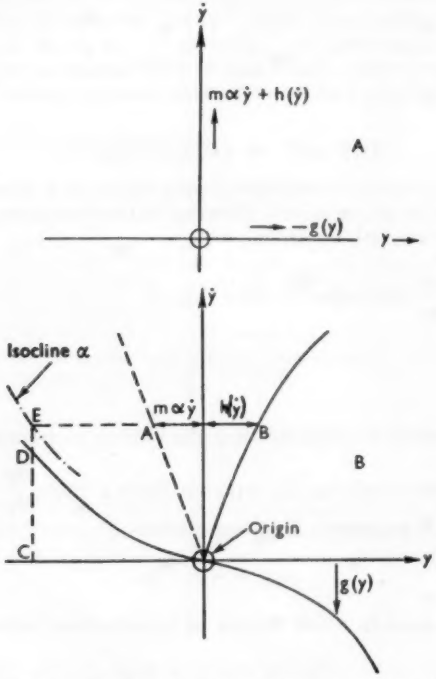


FIG. 12.—Construction for isoclines in cases where superposition holds away.

It is preferable in using this system to know isoclines corresponding to say 5°, 15°, 25° . . . 85°, 105°, etc., and to bridge the gap between the 55° and 65° isocline with a trajectory line at 60°. This will maintain uniform precision throughout the process.

When the elastic part of the system is linear, i.e. $g(y) = Ey$ the construction leads to Lienard's construction described in textbooks on non-linear analysis[12–15] because from Equation (14)

$$y = -\frac{(m\alpha\dot{y} + h(\dot{y}))}{E}$$

which corresponds to the construction.

When the damping part of the system is linear, i.e. $h(\dot{y}) = K\dot{y}$ we have

$$\dot{y} = \frac{-g(y)}{m\alpha + K} \tag{15}$$

and if there is no damping.

$$\dot{y} = \frac{-g(y)}{m\alpha} \tag{16}$$

which is the result used in the case quoted earlier, Equation (3).

Comparison of Equations (16) and (15) shows that the isoclines for the case of a non-linear spring with linear damping can be deduced from the non-linear spring load deflection curve in a manner similar to the no damping case, i.e. the isoclines have the same shape as the spring load deflection curve in a manner

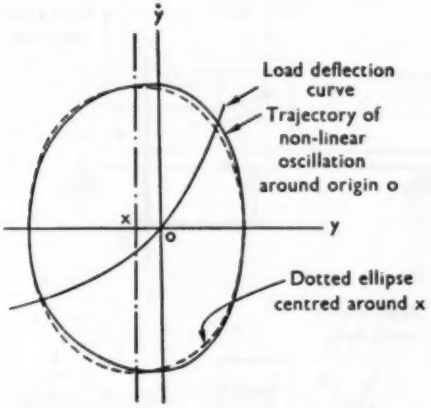


FIG. 13.—An approximate solution (not to scale).

similar to the no damping case, i.e. the isoclines have the same shape as the spring curve but the value of α appropriate to a given isocline is obtained by subtracting K/m from the α of the undamped case.

Approximate solutions.—The study of approximate solutions is also facilitated by the use of Equation (2) on the phase plane. If an assumption of stress-strain characteristics is made then the trajectory in Figure 9 is artificially decided; if the wave form of the driving force is assumed then the relationship between the trajectories of Figures 8 and 9 is artificially decided.

As a very simple example, the assumption of SHM in the case of rubber in compression is like assuming an ellipse in Figure 5 and there are at least three arbitrary constants which arise according to how the amplitudes of y and $\dot{y}$ and the center of oscillation are made to correspond to Figure 13. If the second harmonic is included it would tend to eliminate the gap between the dotted and full lines. In a damped case more arbitrary constants are required in fitting (say) a logarithmic spiral or a related ellipse which is the damped SHM equivalent. A useful study could be made of the methods of interpretation of dynamic tests given in the existing literature in this manner—it would indicate the character of their agreements and disagreements

METHODS OF TEST

Consideration of the analysis presented above will show that in any dynamic test, assumption of form of equation or of motion, driving force or stress-strain may invalidate not only the numerical values of parameters but also the phenomenological interpretation of the experiment.

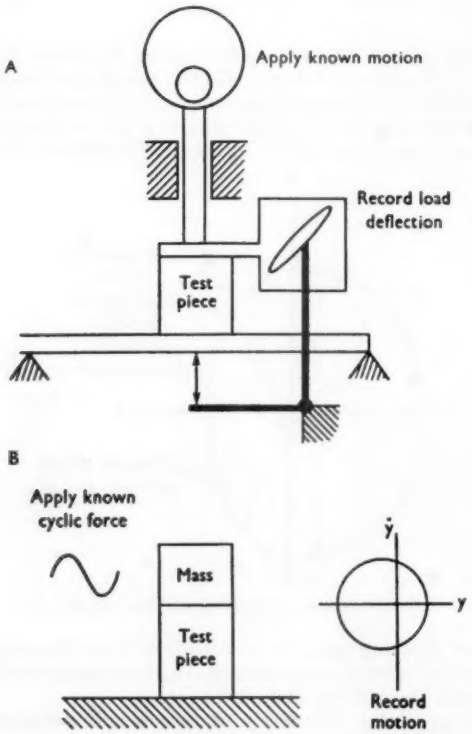


FIG. 14.—Principles of fundamentally sound methods of determining viscoelastic properties.

If the object of a dynamic test is to determine the fundamental properties of a viscoelastic material then it appears that there are only two fundamentally sound ways at present available.

(A) Apply a known motion (displacement and velocity) and measure the resulting viscoelastic reaction as functions of displacement and velocity.
(B) Apply a known fluctuating force (preferably cyclic), record the resulting motion and use Equation (1) (in one of its forms) on a phase plane plot to determine the vicoelastic reactions (see Figure 14).

This is an important conclusion.

Alternative approaches, for example, where cyclic force is applied and a load deflection curve recorded (e.g. the Roelig machine), involve inbuilt assumptions and are not fundamentally sound.

The objective is always to determine the viscoelastic reaction $f(y, \dot{y})$ in terms of displacement y and velocity $\dot{y}$ without any assumption of governing equations. Clearly, the assumption of any form of governing equation reduces the analysis to an empirical one.

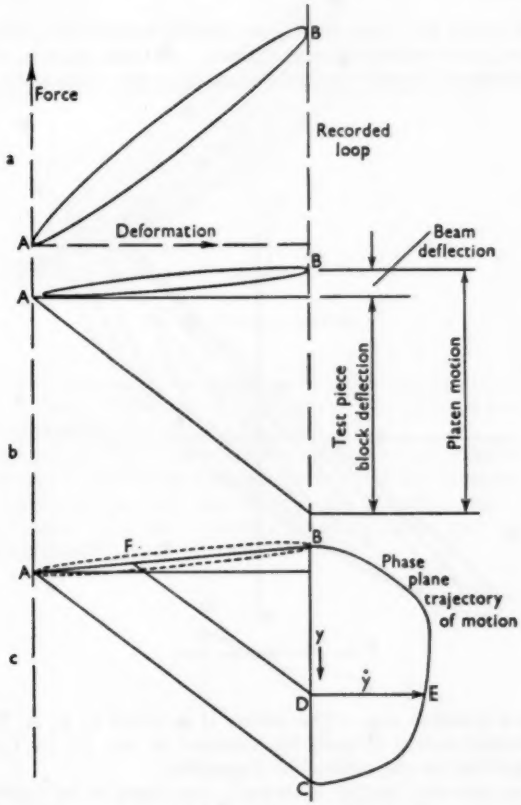


FIG. 15.—Derivation of velocity in case of machine which records force-deflection.

The Davies machine[6, 7, 8] has already been mentioned as operating on method A (see also Appendix 1).

Method (B) above does not seem to have been used to date. Such systems as have been described in the literature and which seem to approximate to (B) do not meet the stringent requirements uncovered by the present analysis.

One method of applying method B would be to record an acceleration-time curve of a freely vibrating system starting from known initial conditions and

produce a phase plane plot of the motion either by:

(*a*) integrating acceleration-time to obtain velocity-time, and again to get the displacement time curve from which data a phase plane plot could be constructed; or

(*b*) to directly draw (graphically) the phase plane plot using the principle given in Figure 10 (see Appendix 3) which also gives the basis of a numerical step-by-step method.

Having obtained the phase plane plot, isoclines would be plotted and conformity to the law of superposition examined. In these cases in which the law appears to hold it will simplify the determination of the viscoelastic laws.

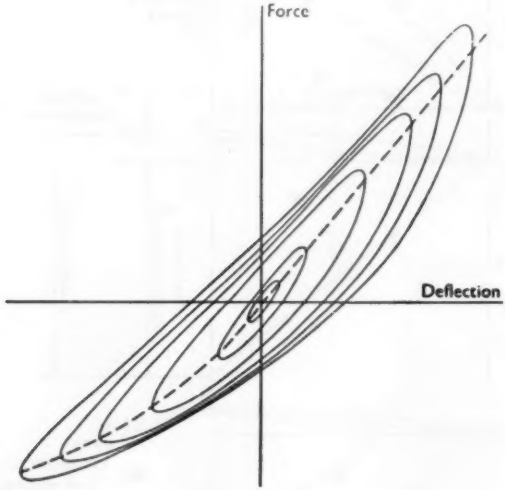


FIG. 16.—Recorded loops.

Curves for a practical case.—The author is indebted to R. A. Ward for the following practical curves (Figure 16) obtained on our Davies type machine. Figure 17 is derived by the method of Figure 15.

Clearly the material (butyl) is strongly non-linear in its elastic and in its damping properties and what is more important, the superposition law does not hold. Recent tests on rubber show similar characteristics.

The damping is not reducible to a simple algebraic expression. The damping "constants" vary with velocity and displacement and differ in the two directions of movement from a given mean deflection. To deal with this case analytically would need a special algebra. No attempt is made to develop this here.

It is possible to deduce the phase plane trajectory of the motion which would result if a known mass is supported by a material whose properties have been determined on a dynamic test machine of type A above (see Appendix 4

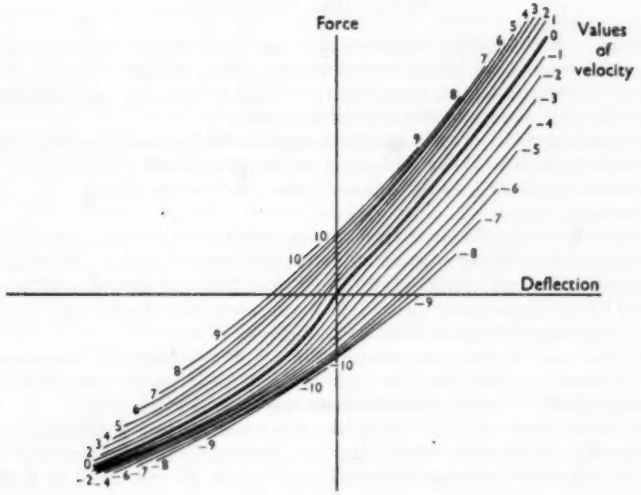


FIG. 17.—Derived properties.

and Figure 18, which show the trajectory under no driving force for the material of Figure 16). Clearly the methods developed in the paper would enable the motion under any driving force to be derived.

Other methods of test.—It is important to note that the alternative approaches of impact methods or of rolling wheels do not avoid the problems under discussion nor do they, as currently described in the literature, meet the requirements set forth here. The use of energy instead of force and deflection does not solve the problems[22].

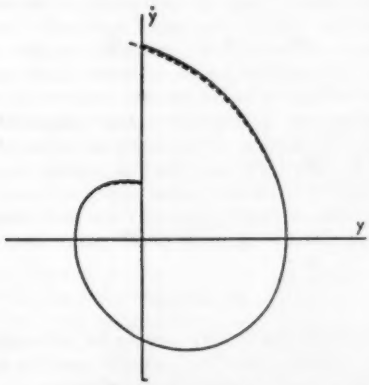


FIG. 18.—Trajectory derived from viscoelastic reactions of Figure 17 (to scale) [full line by method of Figure 21, Appendix 4; dotted line by method of Figures 22 and 23. Note dotted lines are chords, full line is a series of arcs; where dotted line not visible, agreement between two solutions is excellent].

CONCLUDING REMARKS

Rubber and rubberlike materials are non-linear in the widest sense of the word. Not only is the stress-strain corresponding to zero velocity of movement curved, the damping non-linearly related to velocity and displacement, but also the law of superposition does not hold.

In designing tests, or analyzing test data and in discussing rubber vibration behavior in terms of rubber molecular structure the test apparatus or mathematics must not enter into the answer otherwise false explanation will arise for the phenomena.

If any effects are deduced from a test, the test apparatus, procedure and analyses must be critically reviewed before the effect is given a physical name. For example, apparent increase of elastic modulus with decrease of amplitude obtained by the usual linear analysis and apparent greater modulus obtained on dynamic test may be due to erroneous analysis.

This is a rejection as unproved of the commonly held view expressed in a summary paper by Gehman[1], who states "that the dynamic procedure induces a different structure in the material than occurs in a static test".

The phase plane methods employing the basic relation between gradient of the trajectory on the phase plane and the physical quantities, external driving force, viscoelastic reaction and momentum which are discussed in this paper provide a means of studying the problem. They are general and involve no arbitrary assumptions. They can also be used to assess the validity of an approximate analysis.

For ease of presentation it has been implicitly assumed in the discussion in the paper that the viscoelastic reaction is defined by the velocity and displacement and is not dependent on the previous history. The departures from this assumption would be tested by using different kinds of motion instead of SHM in method A (applied motion, recorded force) and by the use of a variety of driving forces in method B (applied force, recorded motion).

Such effects do not invalidate the phase plane approach but would make it more difficult as more factors would need to be considered and this might be equivalent to using a book of curves of viscoelastic reaction curves, reference being made to the appropriate page at each point in the motion.

The important point is that by the use of methods of analysis free from assumptions of mathematical functional forms the test data will ultimately lead to the correct form of assumption to be made in future analysis. When this stage is reached some reduction in the analysis procedure may be permissible, and some form of algebra may be developed; the complexity of this algebra will depend on the physical properties of the materials being studied.

The points raised in the paper show that in order to lead to a true physical interpretation a dynamic test should either apply a known motion and determine the stress-strain data or apply a known force and determine a motion and deduce the stress-strain relationship by phase plane analysis.

SUMMARY

In those cases where dynamic tests are to be interpreted in terms of the molecular structure of rubber, there is a definite need for a method of analysis which is wholly free from mathematical assumptions.

Such a method of analysis is possible by the use of phase planes of velocity plotted against displacement. This is so because the slope of the trajectory

at any point of the motion of any single degree of freedom system can be written solely in terms of physical quantities, namely, driving force, viscoelastic reaction and momentum. The analysis involves no hidden mathematical assumption.

Methods of deriving stress strain relationships from phase plane trajectories are described. This phase plane method is discussed in some detail.

Examples are given showing the inadequacy of the usual linear analysis in the case of rubberlike materials. Analysis shows that dynamic test machines should either apply a known motion and record a force-deflection curve or apply a force of known wave form and record the resulting motion as a phase plane trajectory. If force and motion are not kept independent of each other in this manner there is an inbuilt mathematical relationship which, more often than not, influences and falsifies the results.

An important conclusion is that only when the nature of the non-linearities, or what is the same thing, the character of the functions which correctly describe the actual behavior of a vibrating system have been established by sound analysis of test data, should the phenomena be ascribed to the physical properties of the material.

Because of the important consequence of the acceptance of some common mathematical steps in any analysis, certain of these are critically examined and their relevance discussed.

ACKNOWLEDGMENT

The problems discussed have arisen in the course of work for the Dunlop Rubber Company Ltd. and the author wishes to express his thanks for permission to publish this paper.

APPENDIX 1

Machine test, Method A.—The Davies machine[6, 7, 8] records the load-deflection curve but does not directly record velocity.

A simple and, in many cases, sufficiently accurate means of deriving velocity is shown in Figure 15. The total deflection of the block is reduced by the deflection of the beam. This deflection is small and proportional to the recorded beam load, the errors of this effect are small in a number of practical cases of interest.

If the platen's motion is SHM as in the Davies machine the phase plane trajectory used in Figure 3A is a semi-circle (see discussion of Reference 8).

A more direct method would be to record velocity by an electronic or electromagnetic device.

APPENDIX 2

Direct derivation of phase plane trajectory for non-linear elastic system without damping.—In Figure 19 draw the non-linear stress-strain curve at such a scale that the tangent at the mean position of the oscillation is at 45°. Then from the discussion of Figure 10, the trajectory at e is instantaneously an arc of center d where cd on the phase plane equals the ordinate ab on the stress-strain curve.

If the stress-strain curve is linear it will be found that the phase plane will be a circle struck from the origin O as $fb = ob = oc$, therefore d always coincides

with O. This fact also enables the $\dot{y}$ and y scales to be determined by obvious arguments as the diagram corresponds to resonance in this case.

This construction also enables alternative direct proofs of the points made in relation to Figures 5 and 7.

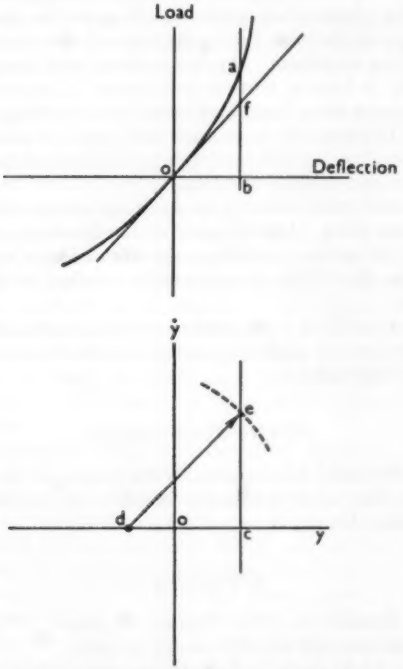


FIG. 19.—Trajectory for non-linear elastic system.

APPENDIX 3

Direct derivation of phase plane plot from an acceleration-time curve.—Let Figure 20*a* represent a recorded acceleration-time curve where the distance of *og* along the abscissa represents unit time and the ordinate represents acceleration. In the time $jk = \delta t$ the acceleration changes from *lj* to *mk* averaging at *hj* over the interval of time *jk*. On the phase plane (Figure 20*b*) the point corresponding to *lj* is *p* and that corresponding to *mk* is *q*, where angle $pnq = \delta t$ in appropriate units (see below) provided the angle is small enough to ignore second order errors which arise if the $\frac{ps}{pn}$ is not small.

Assume the construction has proceeded from the initial starting point step by step to *p*.

Draw *pn*, the perpendicular to the *y* axis, mark off $nr = hj$.

Draw the arc *pq* cutting the line *nq* at *q*. This is then a segment of the trajectory and the process can be carried out step by step from given initial conditions of displacement, velocity and acceleration.

The scales are chosen by using the known fact that a SHM is a circle on the phase plane of appropriate scales and the same circle can be regarded as the locus of a rotating vector which can also be regarded as a vector describing the acceleration at a specific scale.

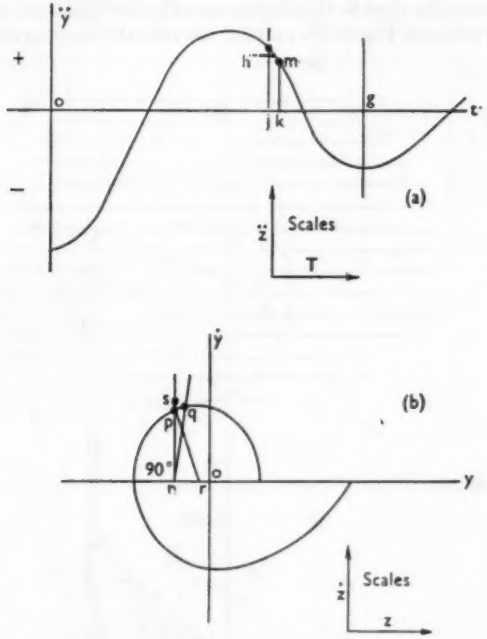


FIG. 20.—Derivation of phase plane trajectory from acceleration time curve.

These scales are defined by

$$\frac{T}{2\pi} Z = \dot{Z} = \frac{2\pi \ddot{Z}}{T}$$

where Z = distance along the y axis representing displacement unit
$\dot{Z}$ = distance along the $\dot{y}$ axis representing unit velocity
$\ddot{Z}$ = distance on the $\dot{y} - t$ chart representing unit acceleration
T = is the periodic time which results in a circular plot on the phase plane, and the radius equal to the ordinate of the acceleration curve.

In the practical application it is convenient to take T as being periodic time *og*, as then departures from SHM can be readily recognized.

Note that to represent the element of time δt, angle $pnq = \dot{Z}dt/\dot{Z}$.

APPENDIX 4

Derivation of phase plane trajectories of free vibrations from load-deflection curves obtained on Davies or similar type machine.—There are two graphical

procedures possible. Analytically they are identical, the differences are purely those of graphical construction:

(*a*) Assume that the process about to be described has been employed and the point *a* on the phase plane trajectory has been reached. Drop a perpendicular *abed* to the displacement axis of the load-deflection curves A derived as in Figure 21, cutting the velocity line corresponding to that

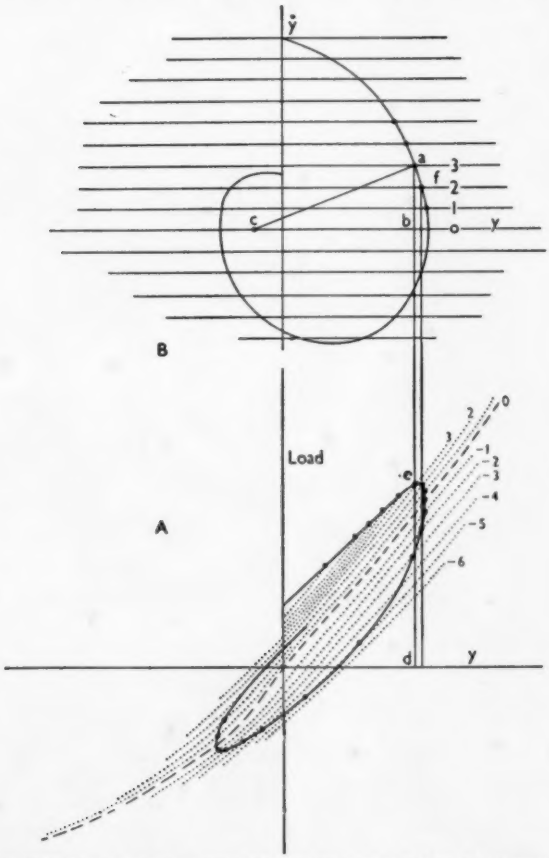


FIG. 21.—Derivation of phase plane trajectory for free oscillation from load-deflection data.

of *a*, at *e*. From *b* mark off $bc = ed/m$ where *m* is the mass. With center *c* strike arc of *af* to the next velocity line, continue the process as if point *f* is point *a*. The required trajectory from a given starting point can be obtained as a sequence of elements *af*.

(*b*) This second process obtains the isoclines from which the trajectories can be obtained. In Figure 22 draw an equispaced grid of radial lines (*A*). Along the *y* axis mark off equispaced steps. To obtain a point on the

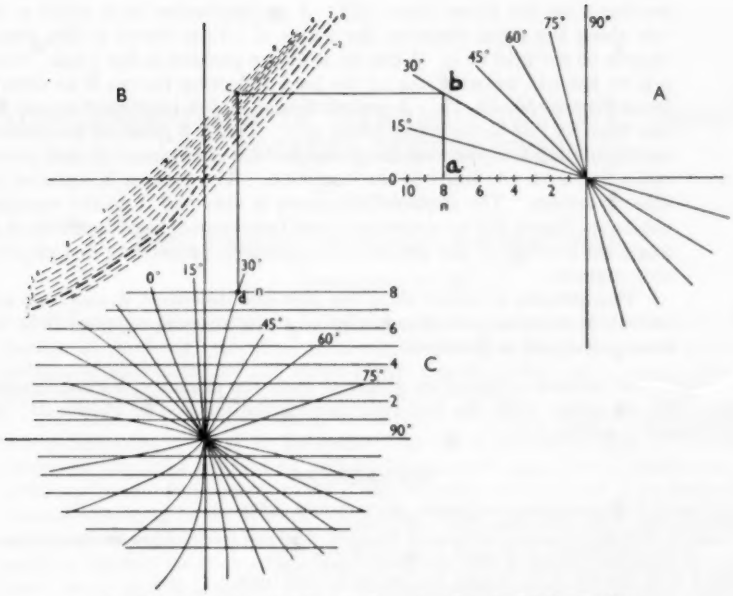


FIG. 22.—Derivation of isoclines on phase plane from load deflection data.

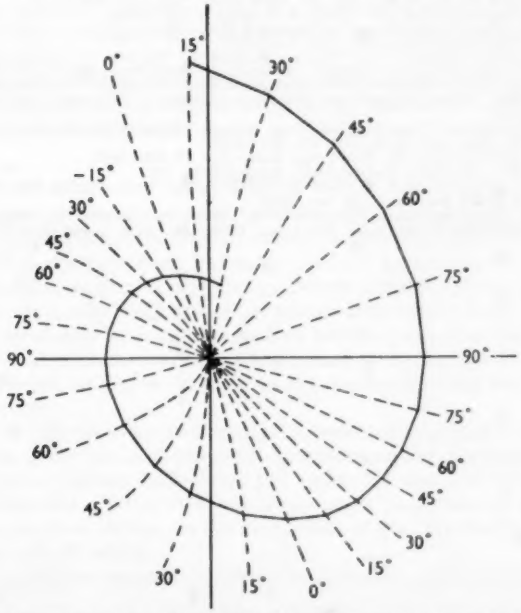


FIG. 23.—Trajectory derived from isoclines produced by the method of Figure 22 (to scale).

isocline α on the phase plane (C). A perpendicular from point a, the nth along the equal steps on the y axis of (A) is drawn to the line of slope α on the grid (A). A line bc, is drawn parallel to the y axis, where c is on the nth velocity line of the load-deflection curves B as derived from Figures 15, 16, 17. A perpendicular $C\ d$ is continued to cut the nth velocity line in the phase plane (C). This is a point on the isocline corresponding to slope α on the phase plane. A sequence of such points using line α on (A) leads to the isocline α. The process is repeated for other isoclines. The required trajectory is obtained from the resulting isoclines (Figure 23) by drawing chords between adjacent isoclines at an angle the average of the values of the isoclines, proceeding in a step-by-step manner.

This process is longer than the first one described if only one trajectory is required but if a family of trajectories is required it is the more rapid and satisfactory.

Figure 23 includes a trajectory obtained from the isoclines; Figure 18 compares this trajectory with the one obtained by the method of Figure 21; the agreement is satisfactory.

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NON-LINEARITIES IN DYNAMIC TESTS II. IMPACT AND ROLLING WHEEL TESTS *

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INTRODUCTION

Viscoelastic properties of rubberlike materials are currently studied by a number of methods: vibration methods involving a single degree of freedom system, measurement of the stress-strain curves under cyclic application of deflection, impact tests and tests using rolling wheels.

The effect of non-linearities on the motion of a single degree of freedom system is discussed in detail in Reference 1 and it is concluded that the analysis employed must not contain an arbitrarily assumed equation of motion nor an arbitrary stress-strain relationship if the objective of the tests is to determine the true character of the viscoelastic properties and to relate these to the molecular properties of the material. The character of the viscoelastic properties must be derived from experiment by methods free from inbuilt mathematical assumptions and it is shown that phase plane analysis can be adapted for that purpose.

It is also noted in Reference 1 that measurement of the stress-strain properties during cyclic application of deflection is free from inbuilt mathematical assumptions.

The question which is examined in this related paper is whether the study of impact tests and rolling wheels using energy methods is subject to similar and/or other necessary conditions.

IMPACT TESTS

Consider two masses in collision. It is shown in the appendix that although the energy loss and the coefficient of restitution are mathematically independent of the frame of reference from which the velocity measurements are made, the resilience, defined as the ratio of energy before collision and energy after collision, is not. It is only when one of the masses is infinite and the frame of reference taken as at rest with respect to this infinite mass that resilience (as defined in the rubber literature) equals the square of the coefficient of restitution. In all other cases, resilience depends on the masses involved and the choice of axes of reference.

While it is difficult to prove the point, it seems most probable that coefficient of restitution is the physical property dependent on the viscoelastic characteristics and that resilience depends on the method of test and its apparent constancy is empirical. Otherwise, the viscoelastic properties of a material depend, amongst other things, on the magnitude of the (arbitrarily chosen) mass of the object which hits it.

On comparing the impact of a rubber block rigidly attached to the ground by

* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 36, pages 195–201 (1960).

a moving rigid mass (such as a pendulum) with that of a rubber ball hitting a rigid floor, it will be found that they are not identical cases. In the latter case it is possible for each part of the ball to lose its velocity and energy gradually to zero up to the point of maximum deflection. In the other case the surface layers have either to execute a discontinuous jump to the same velocity as the pendulum and so acquire energy in a discontinuous jump involving an infinite force, or the surface layers are accelerated acquiring kinetic energy from the pendulum which energy is later passed to the rubber to help achieve the maximum strain energy.

The actual surface of impact is at rest in relation to the axes of reference from which the energy is measured (the mass center of the system) in the case of the bouncing ball and in the other case it is not. It is difficult to say whether this difference is important or not as a valid general analysis is difficult and is not attempted here. It suffices to show that apparently equivalent systems are not always equivalent and careful examination must be made when considering whether two systems are equivalent and as to whether they should yield identical test results.

Attempts to determine the dynamic deflection curves from free impact tests by plotting input energy against the maximum deflection which results, require an assumption of functional form of viscoelastic behavior for the determination of the elastic constants. This follows from the reasoning set out in the section "consequences of choice of functional form of equation" in Reference 1 or from the discussion of Figure II of Reference 2.

As would be expected from these arguments, actual tests show that the estimates of peak load are subject to serious errors when derived by the process of differentiating the energy-displacement curve to obtain the load-displacement curve. The mathematics correspond to a fallacious physical interpretation.

It is clear that to deduce the loads developed during impact a knowledge of the stress-strain characteristics is required and that all the points made in Reference 1 apply in regard to such an analysis.

Phase-plane methods can be used to analyze the motion arising in impact tests in a manner identical to that described in Reference 1 for vibrating systems.

ROLLING WHEEL TESTS

In the case of rolling wheels with a rubber tire, published analyses have an arbitrarily chosen stress-strain functional form—although it may be difficult to identify and isolate the assumption within the analyses[3, 4].

That some assumption must be present can be seen from the following discussion. Consider the simplest case where the tire is assumed to be a number of radially disposed non-linear springs equally spaced around the wheel and that each spring deflects in a radial direction only and acts independently of its neighbors. This is much too simple an assumption to be regarded as a full analysis, for in a practical case not only does the material in the same plane normal to the wheel axis affect its neighbors in that plane but also the axial width of the rubber tire affects the behavior. However, this simplifying assumption does not in any way invalidate the relevance of the point about to be made.

Each spring passes through the same range of stress from zero prior to entry in the contact region to a maximum at or near the center of contact, returning to zero after passing through the contact region. The losses during this cycle can be determined by measuring the torque to drive the system. The

actual input energy to the system or to a given spring, is settled by the stress-strain relation, the geometry of the deflection relationship in the contact region between tire and drum on which it rolls, and the maximum deflection. The stress-strain relationship is unknown.

The load carried by the "tire" is the sum of the components in the direction of the line joining wheel and drum axes of the instantaneous spring reactions of the several springs in the contact region one of which is substantially at its maximum deflection and is at the point of reversal of deflection, and all the others are at an intermediate deflection and moving at a velocity of deflection dependent on the geometry of the system and the location in relation to the line joining the wheel and drum axes.

The applied load is therefore an integral in relation to the peak intensity of stress arising in the cyclic deformation. Hence, in relation to the applied load, the peak stress is a differential and it follows from the arguments in References 1 and 2 that its estimation from a knowledge of applied loads is inaccurate and is dependent on the choice of the functional form of the stress-strain relationship employed in the analysis. The point is similar to that made above for impacting bodies. Clearly the estimation of input energy from measurements of applied load is dependent on the functional form initially assumed for the stress-strain relation.

Furthermore a study of changes in maximum deflection with change of applied load is not a reliable means of determining the input cycle or the laws governing the input cycle: this also follows from the arguments in the references quoted.

It follows that while the use of a rolling wheel to determine losses may be free from criticism, attempts to deduce the basic stress-strain laws or to estimate the input cycle and relate losses to the input can only be classed as empirical as the analyses involve an *a priori* assumption and this does not meet the stringent requirements set forth in Reference 1. For empirical or practical tests the analyses may be satisfactory; for determining the true physical and molecular properties of rubber, they are unsatisfactory.

CONCLUSIONS

Neither the use of rolling wheels nor impact systems resolves the problems arising from non-linearities in the stress-strain curve of the rubber whose properties are required to be investigated. Measurement of integrated effects such as energy or load carried by a tire on a drum does not directly permit the determination of the magnitude of the peak force developed nor of the character of the viscoelastic reactions.

The problems to be solved are more complex than those found necessary to be discussed in relation to vibration or cyclic test methods[1]. Rolling wheels and impact tests in which energy values are measured are more suited to empirical comparison of properties of rubber than a fundamental understanding of the rubber physical properties such as is required when these properties are to be related to the molecular structure of the material.

SUMMARY

Resilience values determined from impact tests depend on the frame of reference from which the velocities are measured. Only in the case where one mass is infinite and the frame of reference is fixed in relation to this infinite mass is the resilience equal to the square of the coefficient of restitution.

Information regarding changes of energy during impact tests does not lead directly to the determination of the dynamic stress-strain properties of rubber without some assumption of the character of the stress-strain relationships.

Studies of rolling wheels also involve assumptions of the form of the stress-strain relationships which are not deducible from the same experiments.

It is concluded that impact tests in which the energies are the quantities investigated and rolling wheel tests are more suited to empirical comparison of dynamic properties than a fundamental understanding of dynamic properties of rubberlike materials and their relationship to the molecular properties. The use of energy does not resolve the problems arising due to non-linearities discussed in Part I of the paper.

ACKNOWLEDGMENT

The problems discussed have arisen in the course of work for the Dunlop Rubber Company Ltd. and the author wishes to express his thanks for permission to publish this paper.

APPENDIX

COLLISION OF MASSES

Consider two masses in collision.

Let the velocity of the center of gravity of the system with respect to the frame of reference of the observer be C, and it is constant as no other forces act on the system, it being assumed that the impact is in a horizontal line and is a free impact.

Mass	m_1	m_2
Initial velocity	$u_1 = C + X_1$	$u_2 = C + X_2$
Final velocity	$V_1 = C + Y_1$	$V_2 = C + Y_2$
Velocity of approach	$u_1 - u_2 = X_1 - X_2$	
Velocity of recession	$V_1 - V_2 = Y_1 - Y_2$	

It can be shown that

$$C = \frac{m_1u_1 + m_2u_2}{m_1 + m_2} = \frac{m_1V_1 + m_2V_2}{m_1 + m_2}$$

Original

$$KE = \frac{m_1u_1^2 + m_2u_2^2}{2} = \frac{m_1(C + X_1)^2 + m_2(C + X_2)^2}{2}$$

$$= \frac{(m_1 + m_2)C^2}{2} + (Cm_1X_1 + m_2X_2) + \frac{m_1X_1^2 + m_2X_2^2}{2}$$

$m_1X_1 + m_2X_2$ is zero for the following reason. The velocity of m_1 relative to the *cg* is X_1 and that of m_2 is X_2. Hence at unit time before the impact the mass m_1 is at a distance $-X_1$ from the *cg* and mass m_2 is at a distance $-X_2$ from the *cg*. Therefore $-m_1X_1 - m_2X_2 = 0$ as this defines the *cg*. Hence:

$$\text{Original } KE = \frac{(m_1 + m_2)C^2}{2} + \frac{m_1X_1^2 + m_2X_2^2}{2}$$

= sum of KE of the system if there is no relative movement between the masses and the KE of the masses due to initial velocities relative to the *cg*.

= External KE + Initial Internal KE.

$$\text{Final KE} = \frac{m_1V_1^2 + m_2V_2^2}{2} = \frac{m_1(C + Y_1)^2 + m_2(C + Y_2)^2}{2}$$

$$= \frac{(m_1 + m_2)C^2}{2} + \frac{m_1Y_2^2 + m_2Y_2^2}{2}$$

= External KE + Final Internal KE.

From the above it follows that loss of

$$\text{KE} = \frac{m_1(X_1^2 - Y_1^2)}{2} + \frac{m_2(X_2^2 - Y_2^2)}{2}$$

Which is independent of C the velocity of the center of gravity of the system.

Resilience is commonly defined as the ratio $R = \dfrac{\text{Energy after impact}}{\text{Energy before impact}}$ and in the case of a system of the colliding masses this is commonly defined as

$$R = \frac{\text{Final value of the KE of the system}}{\text{Initial value of the KE of the system}}$$

without clear specification of the axes of reference from which the energies are measured.

If we put A = External Energy
B = Initial Internal Energy
D = Final Internal Energy

using the terms defined earlier, we have:

$$R = \frac{A + D}{A + B} \quad \text{and} \quad r = \frac{D}{B}$$

where r is the Intrinsic Resilience or resilience of a system with reference to axes located at the center of gravity of the system of impacting masses.

R and r can be expressed in terms of L, the loss of kinetic energy at impact

$$R = 1 - \frac{L}{A + B}$$

and

$$r = 1 - \frac{L}{B}$$

The relation between R and r can be written

$$R = \frac{\frac{A}{B} + r}{\frac{A}{B} + 1} = \frac{A + Br}{A + B}$$

This can be also written

$$r = R - (1 - R)\frac{A}{B}$$

or

$$\frac{1 - r}{1 - R} = \frac{A}{B} + 1$$

Where R is the resilience referred to a system of axes with reference to which the *cg* of the system of impacting masses move with a constant velocity C. It should be noted that the relation between the values of r and R depends solely on the ratio of the "internal" and "external" energies and not on the losses.

It is clear then, that in general, the motion of the axes of the reference influences the estimate of resilience even though the estimate of energy loss is independent of the motion of the axes of the reference.

The difficulty is somewhat akin to those arising in the choice of input energy when trying to assess energy loss ratio or resilience from stress-strain loops.

Limiting case of one infinite mass.—In the limiting case where one mass is infinite and infinitely rigid and the energies are measured from axes fixed to this infinite mass we have the case of the axes coincident with the center of gravity of the system and hence $A = O$ and $R = r$. The resilience measured is in this case, the intrinsic resilience as defined. It is essential that the assumption of infinite rigidity holds in this case.

Coefficient of restitution.—Let

$$\epsilon = \text{Coefficient of restitution.}$$
$$= \frac{-\text{ Relative Velocity of recession}}{\text{Relative Velocity of approach}}$$

The negative sign is needed to make ϵ positive and yet keep other signs correct. Then

$$\epsilon = -\frac{(Y_1 - Y_2)}{(X_1 - X_2)}$$

which is independent of frame of reference as $X_1 - X_2$, etc., are relative velocities.

Hence no problems arise due to axes of reference in the case of coefficient of restitution.

Connection between restitution and resilience.—As already defined

$$r = \frac{m_1 Y_1^2 + m_2 Y_2^2}{m_1 X_1^2 + m_2 X_2^2}$$

and

$$\epsilon = \frac{(Y_1 - Y_2)}{(X_1 - X_2)}$$

Clearly there is no simple universal relation between these two quantities; it also follows that R and ϵ are not simply related.

It also follows that the usual statement that resilience equals the square of the coefficient of restitution is true only if one of the masses is infinite and the resilience is the intrinsic resilience r or stated another way the resilience equals the square of the coefficient of restitution is true only if one of the masses is infinite and the axes of reference from which the velocities are measured to calculate the resilience R are fixed in relation to the infinite mass i.e. $r = \epsilon^2$ if one of the masses is infinite and $R = \epsilon^2$ if one of the masses is infinite and velocities are measured in relation to that particular mass. Otherwise neither r nor R equal ϵ^2.

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ADHESION OF HIGH POLYMERS. VI. THE EFFECT OF MOLECULAR WEIGHT OF NBR COPOLYMERS OF VARIOUS POLARITIES ON ADHESION TO POLAR AND NONPOLAR MATERIALS *

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The dependence of adhesion of polymers on molecular weight and polarity has been established[1] in experiments with commercial polyisobutylene (PIB) of varying molecular weights and butadiene-acrylonitrile rubber (NBR) with different percentages of acrylonitrile units. However, the relative effects of molecular weight and polarity in these experiments could not be established definitely because of their mutual influence on the adhesion. Therefore it was of considerable interest to make clear the influence on the adhesion of (1) the molecular weight at constant polarity and (2) polarity at constant molecular weight. In addition, it was found interesting to investigate the temperature dependence of adhesion for individual fractions of polymers of various polarities.

Fractions of commercial nitrile rubbers SKN-18, SKN-26 and SKN-40 were used for this work as adhesives. Polar polyamide (capron film perfol PK-4) and nonpolar polyisobutylene of molecular weight ~118,000 were used as substrata.

Fractional precipitation[2, 3] was used to separate rubbers into fractions. The polymers were precipitated from 4–5% benzene solution at room temperature using methanol as a precipitant. The molecular weight of the fractions was determined by the light scattering method[4-6].

The results of measurement of the molecular weight of fractions and their relative proportions are shown in Table 1. The content of acrylonitrile units was computed for each fraction based on nitrogen content determined by the Dumas method[7]. The data in Table 1 show that the nitrile content in each fraction of NBR changed only slightly and can almost be considered constant.

Samples for determination of the adhesivity of the polymer fractions under consideration were prepared by the method described elsewhere[8].

Some of the samples bonded at room temperature were heated under load in the oven at temperatures of 50°, 100°, 150°, 175,° and 200° C for 30 minutes. After cooling to room temperature, the samples were peeled at a constant rate (0.3 cm/sec) on a dynamometer ZNIKS. Unheated samples were tested 30 min after preparation. The results of testing are expressed quantitatively as peeling strength of bonded specimens in g/cm. All values of peeling strength are averages of 5–8 parallel measurements.

During testing of bonded specimens observations as to the type of separation were made. It is possible to judge the nature of separation by means of adhesiograms, which were obtained from testing of each bonded specimen. Re-

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TABLE 1

PROPERTIES OF NBR FRACTIONS

Polymer	Fraction	Molecular weight	Amount of Fraction, % by weight	N, %	Nitrile content, %
SKN-18	1	334,000	5.1	5.1	19.3
	2	278,000	3.4	5.32	21.2
	3	250,000	44.9	5.23	19.8
	4	100,000	33.9	6.13	23.2
	5	25,800	12.7	—	—
SKN-26	1	408,000	4.9	8.21	31.0
	2	364,000	30.5	8.49	31.0
	3	340,000	50.0	8.63	32.6
	4	238,000	14.6	8.66	32.8
SKN-40*	1	550,000	31.3	11.55	42.2
	2	524,000	6.2	11.22	42.5
	3	378,000	22.3	11.25	42.2
	4	266,000	31.3	11.62	44.0
	5	100,000	8.9	10.8	41.0

* In addition to these five fractions a sixth fraction of copolymer SKN-40 was used. It was obtained in another experiment and was not taken into account in the calculations of Table 1. Its molecular weight is about 20,000.

sults are shown in Figures 1–5 and in Table 2. The solid curves correspond to adhesive failure, dotted to cohesive failure of bonded specimens.

Adhesion of butadiene-acrylonitrile copolymers to a polar surface (polyamide). Effect of molecular weight on adhesion.—The data of Figure 1 show that at room temperature contact the adhesion of NBR to polyamide decreases with increasing molecular weight. At this temperature, the adhesion of fractions having a molecular weight of more than 300,000–350,000 is very small and is nearly constant.

The same behavior was observed earlier for autohesion (self-adhesion) of PIB specimens of different molecular weight[11] and of their adhesion to cellulose[1], and for the autohesion of polyisoprenes[12]. The regularity observed is readily explained in the light of the diffusion theory of adhesion[1, 13, 14]. When the molecular weight is low and the size of the macromolecule is commensurable with the segment length, the number of free ends is relatively great, and consequently the probability of their diffusion into a substratum is also great. In keeping with purely steric reasoning, the probability of diffusion of the end

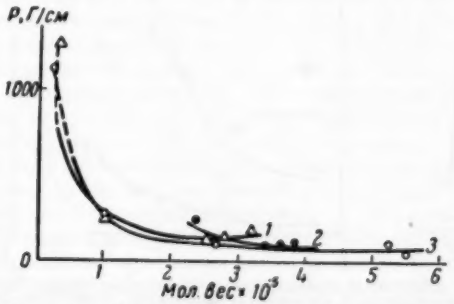

FIG. 1.—Adhesion of the fractions of butadiene-acrylonitrile rubber to polyamide vs. molecular weight. Contact temperature 20° C. *1*—copolymer SKN-18; *2*—SKN-26; *3*—SKN-40.

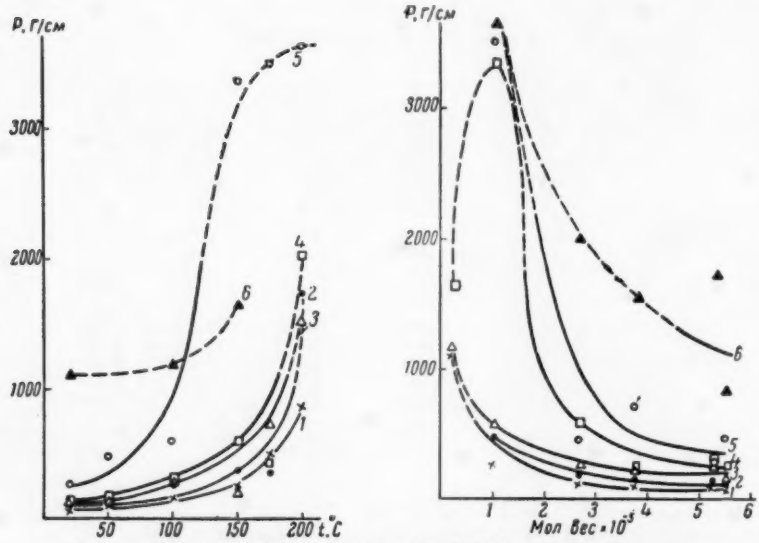

FIG. 2.—Adhesion of the fractions of nitrile rubber SKN-40 vs contact temperature. Figures on the curves correspond to the number of fractions.

FIG. 3.—Adhesion of copolymer SKN-40 to polyamide at different contact temperatures vs molecular weight. *1*—20° C; *2*—50° C; *3*—100° C; *4*—150° C; *5*—175° C; *6*—200° C.

segments into a polymer is more than that of the middle segments. Therefore, under these conditions the adhesion will be determined almost completely by the diffusion of the free ends of the macromolecules. As the molecular weight increases, the relative proportion of end and middle segments changes in favor

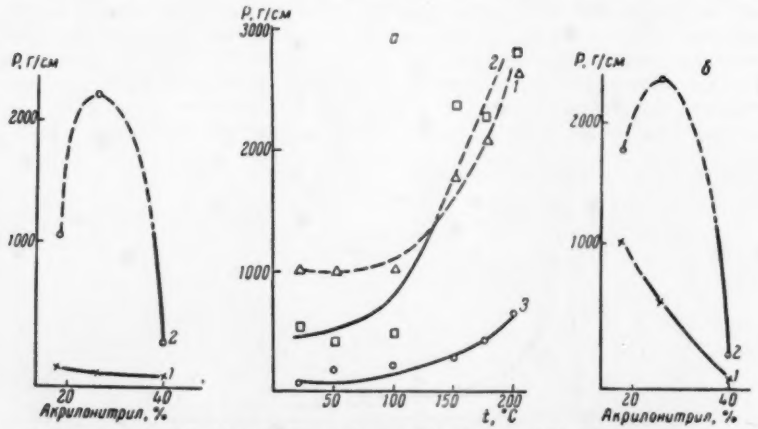

FIG. 4.—Adhesion of fractions of nitrile copolymers with molecular weight of 320,000 at different contact temperatures vs. the content of polar groups. *1*—20° C; *2*—150° C.

FIG. 5.—Adhesion of commercial (non-fractionated) nitrile rubbers to polyamide (a) (left) vs. the contact temperature; *1*—copolymer SKN-18; *2*—SKN-26; *3*—SKN-40. (b) (right) vs. the content of the polar component at various contact temperatures; contact temperature *1*—20° C; *2*—150 °C.

of the latter, thus decreasing adhesion. Finally at some definite value of molecular weight (300,000–350,000) the number of ends of macromolecules becomes so small in comparison with the total number of segments that the participation of the former in diffusion and consequently in the interaction between diffused ends and substratum becomes imperceptible.

Hence, at high molecular weights the adhesion will be determined mainly by the diffusion of middle segments, and in so far as the size of the segments does not depend on the length of the macromolecule, the adhesion ceases to be dependent on the molecular weight of the polymer.

Such an approach is supported by the fact that Bueche, Cashin and Debye[15] could measure the rate of self-diffusion in polybutyl-acrylates only for those of a molecular weight below 300,000. Also it is of importance that Bueche[16] notes the special role of chain ends in phenomena related to the flow and self-diffusion in the bulk polymer. He believes that chain ends serve to loosen the structure of the polymer.

TABLE 2

ADHESION* OF FRACTIONS OF NITRILE RUBBER TO POLYISOBUTYLENE AT DIFFERENT CONTACT TEMPERATURES (G/CM)

Polymer	Fraction	Contact temperature ° C					
		20	50	100	150	175	200
SKN-18	1	80	100	70	60	50	60
	5	35	50	35	50	50	80
SKN-26	1	65	80	130	140	120	110
	4	75	75	100	85	60	60
SKN-40	1	65	50	70	90	80	50
	5	70	50	40	50	40	90

* All data reported correspond to adhesive failure.

The dependence of adhesion on molecular weight can be interpreted following Bueche's point of view that a self-diffusion coefficient is approximately inversely proportional to the viscosity coefficient[16]. Because of this, adhesion under contact time must decrease with increasing molecular weight just as the viscosity of polymer increases.

Increasing the temperature of heat treatment of specimens will influence adhesion to a considerable extent. This is possible to see, for example, from Figure 2 which shows the dependence of adhesion on the temperature of the heat treatment of bonded specimens prepared for polymer SKN-40. This case is a good illustration especially because these specimens display adhesive failure for the majority of experimental points. This figure shows that the general trend of the change of adhesion with increasing temperature is the same for all fractions—adhesivity increases with increasing temperature. It is important that fractions 1–4 show cohesive failure only at temperatures above 180–200° C. This can be explained by the fact that above this temperature (which approximately corresponds to the melting temperature of polyamide[14] the mutual diffusion of adhesive into a substratum and vice versa begins to take place. It causes the striking increase of adhesion and the cohesive failure of a bonded specimen. In contrast, the specimens obtained with the 6th fraction of copolymer SKN-40 show cohesive failure for all temperatures of thermal treatment. This phenomenon can only be explained by the very low molecular

weight (~20,000) of this fraction allowing easy diffusion into a substratum and therefore high adhesion.

Figure 3 represents the same experimental data as the dependence of adhesion on molecular weight at different temperatures of thermal treatment of bonded specimens. In this case the increase of adhesion with temperature is easily seen. From the comparison of this figure with Figure 1 it is possible to conclude that increasing contact temperature increases the adhesion much greater for low molecular weight fractions than for high molecular ones. This is possible to explain by the fact that the activation energy of diffusion of the molecular chain ends is considerably lower than that of the middle segments of the macromolecule.

Curve *6*, Figure 3, is very typical. It shows the change of adhesion of SKN-40 with increasing molecular weight at 200° C, the approximate melting temperature of polyamide. This curve is the highest of Figure 3 and is almost completely characterized by adhesive failure of the bonded specimen. It should be noticed that for copolymers SKN-18 and SKN-26 the change of bond failure from adhesive to cohesive is observed at temperatures much lower than the melting temperature of polyamide. Also the lower the molecular weight of the fraction, the lower are the temperatures of change. From our point of view such a phenomenon can be explained by the lower polarity and therefore smaller intermolecular interaction of these polymers promoting the thermal motion and diffusion into a substratum. As a result the adhesive strength can surpass the cohesive strength even at comparatively low contact temperature. This will be further explained below during consideration of the influence of polarity of the adhesive on adhesion.

The rise of adhesion with increasing contact temperature is readily understandable. First, the increase of temperature increases the probability of activation of segments, allowing easy movement through "a hole", thus readily increasing the rate of diffusion. Secondly, as the temperature increases, a greater number of segments of a separate macromolecule gradually become involved in diffusion. At the flow temperature of the polymer the movement of the whole macromolecule becomes possible. This, of course, has to lead to a sharp increase of adhesion. Thirdly, it is known that the size of kinetically active segments decreases with temperature. Smaller segments will diffuse into a substratum more readily thus promoting the adhesion. Finally, as the temperature increases it becomes necessary to take also into account the changes which occur in the structure of the substratum. The substrate becomes softer and more friable. The size of microvoids or imperfections of structure increases leading to a rise in the rate of diffusion and the depth of the penetration of macromolecules of adhesive diffusing into substrate. Also at temperatures above the melting temperature of crystalline substratum considerable diffusion of segments of macromolecules of substratum into adhesive becomes possible. It is understandable that when both components of the bonded specimen (adhesive and substratum) are in a stage of flow the motion of macromolecules as a whole can take place during diffusion. This probably occurs for the SKN-40-polyamide pair at the contact temperature of 200° C. The sharp increase of the slope of the adhesion temperature curves in the region of change from adhesive to cohesive failure supports such a change in character of diffusion. This is shown very well in Figure 2.

As contact temperature is increased, the transition from adhesive failure to cohesive for bonded specimens of NBR with polyamide is always observed as a result of the increase of diffusion and consequently of the increase of adhesion.

Such a transition is reached at a lower temperature when the molecular weight of the fraction is lower. For instance, for SKN-18 the temperature at which the stripping acquires cohesive failure if 150° C for the 1st fraction (the highest molecular weight), 100° C for the 2nd and the 3rd fractions the molecular weights of which are slightly different, 50° for the 4th fraction, and 20° for the 5th fraction (the lowest molecular weight). Such a dependence could be easily explained by the fact that the cohesive strength of a polymer decreases with decreasing molecular weight. However, we cannot see such regularity from the results of testing. Probably, the peeling strength under cohesive failure of the bonded specimen characterizes the true cohesive strength of a polymer to a small extent. Further, cohesive strength of the bonded specimens for a definite fraction appears to be constant for all contact temperatures. Such constancy, however, was not discovered in the experiment reported.

The observed nonmonotonic change of the cohesive strength of bonded specimens heated at different temperatures is probably connected with the process of degradation and crosslinking of NBR.

The investigation of the cohesive strength of nitrile rubbers with the change of contact temperature was not within the scope of this work. However, low molecular fractions showed more ability to increase cohesive strength (crosslinking) with increasing contact temperature than high molecular fractions. In the high temperature region the copolymer with the average nitrile content (SKN-26) showed a decrease in cohesive strength. The presence of the maximum on the curve 4 (Figure 3), representing the change of adhesion of copolymer SKN-40 as a function of molecular weight at 150°, probably can be explained by such changes of cohesive strength.

The effect of polarity of fractions of NBR on adhesion.—It can be seen from Figure 1 already that at the room temperature, the adhesion of fractions of NBR of different molecular weight to the polyamide slightly depends upon the content of nitrile groups.

Figure 4 represents data characterizing the adhesion of NBR to polyamide at 20 and 150° C vs the content of nitrile groups. In order to exclude the influence of molecular weight on adhesion as assumed fraction of molecular weight 320,000 was chosen for polymers of different polarity (in this region of molecular weight, as can be shown from Figure 1, its change has very little influence on the values of measured adhesion). The values of adhesion of copolymers to polyamide were taken from the curves characterizing the dependence of adhesion of different fractions on molecular weight at contact temperature 20 and 150° C. On the basis of Figures 4 and 1, one may conclude that at room contact temperature the adhesion of copolymers to polar substratum depends to a small degree on the content of polar groups in the copolymer. However, at contact temperature the adhesion depends on the polarity to a great extent. The copolymer SKN-40 shows minimum adhesion in this case. The bonded specimens of SKN-18 and SKN-26 have cohesive failure and reasonably high peeling strength. This proves their much higher adhesion to polyamide.

On the basis of these data the following conclusion may be drawn; the less polarity a polymer has, the greater its adhesion will be in the case of an increase in the contact temperature. This is confirmed, for example, by that fact that the transition of adhesive to cohesive failure was observed at higher temperatures when the polarity of a polymer was greater. For the bonded SKN-18 specimen at the contact temperature 100° the mixed character of failure could be observed only for one fraction; at the same time for another four fractions cohesive failure was obtained; and for all fractions of copolymer SKN-26 the cohesive failure was

reached after heating only to 150°; and as far as copolymer SKN-40 is concerned even after thermal treatment at 200°, one fraction showed adhesive failure.

The reason for the lower adhesion of nitrile copolymer with a high content of polar groups might be explained by poor compatability with polyamide or by the fact that the diffusion of this polymer into the substrate becomes difficult because of the rigidity of their molecules and of the presence between them of intermolecular forces of considerable value. In the first case lower adhesion would be explained by a thermodynamic factor. In the second case it would be explained by a purely kinetic effect. In order to check which of these assumptions is correct the swelling of samples of all copolymers used was determined in caprolactam which is the monomer of this polyamide. In-so-much as caprolactam[17] melts at 69–71° C the swelling experiments were made at 80°. Since the crude nitrile copolymers are soluble under these conditions, they were vulcanized before swelling up to the same degree of crosslinking. In accordance with experimental data the vulcanized copolymers after being in monomer for 26 hours at 80° C had the following degree of swelling (% by weight); SKN-18—325, SKN-26—465, and SKN-40—480.

From the fact that the NBR polymer with maximum swelling in caprolactam must have a polarity closer to that of polyamide than do the others, we can conclude that copolymer SKN-40 has the best compatability with polyamide. The correctness of the conclusion is supported also by comparison of the values of the specific cohesive energy[18] of the copolymers discussed: SKN-18—9.30, SKN-26—9.50, SKN-40—9.83, and polyamide—15.05 $(cal/cm^3)^{\frac{1}{2}}$. Hence, cohesive energy of copolymer SKN-40 is closer to that of polyamide and in accordance with the contemporary approach it must cause the best compatability for this pair of polymers under similar conditions. Therefore, the maximum increase in the low nitrile content copolymer to polyamide should be explained from a purely kinetic point of view. It is obvious that the increase of flexibility of molecular chains and the destruction of intermolecular links take place with increasing temperature more rapidly for less polar SKN-18 or SKN-26 adhesive than for the more polar adhesive SKN-40.

The fact that less polarity butadiene-acrylonitrile copolymers show higher adhesion as compared to copolymers of higher polarity can serve as a satisfactory proof of the diffusion theory of adhesion. The adsorption theory cannot explain such a phenomenon—according to it, the adhesive strength can increase only with the decrease of the difference between polarity of adhesive and substratum.

Adhesion of unfractionated butadiene-acrylonitrile copolymers.—It appeared to be of interest to compare the adhesion of individual fractions of nitrile copolymers with that of unfractionated commercial products. For the purpose of this investigation the bonded specimens of nonfractioned copolymers were prepared and tested as described above. Before testing, the bonded specimens were heated to different temperatures as was done in the case of the bonded specimens of individual fractions. Results of the experiments are represented by Figure 5 (*a*, *b*) which show the change of adhesion of nonfractionated copolymers to polyamide vs the contact temperature and the polarity. As can be seen from these data the adhesion decreases also with an increasing content of the polar group in the copolymer. The same influence of the content of polar groups in the copolymer on the adhesion to a polar substratum (cellophane) was found earlier for nitrile copolymers[1].

As a result of comparison of data of the individual fractions of copolymers

with those of nonfractionated rubbers, one can see that in the case of the former the adhesion has a very slight dependence upon the polarity of the adhesive, but in the case of the latter the abrupt fall of the bond strength with the increase of acrylonitrile units in the copolymers seems to exist. However, this contradiction is only apparent and can be explained very easily if one takes into account the content of fractions of different dispersity in commercial rubbers. The data of Table 1 show that unfractionated nitrile rubbers have a very great difference in the amount of high and low molecular fractions. Thus the amount of fractions with a molecular weight less than 250,000 is 91.5% for SKN-18; 14.6%—for SKN-26 and 8.9%—for SKN-40. Hence the reason for the large decrease of adhesion in this set of polymers is not due to the increase of their polarity, but due to the decrease in the content of low molecular weight fractions which influence to a great extent the adhesion of the polymers as it was shown before.

As can be seen by comparing the curves *2* and *2* (Figures 4 and 5b), for fractions with molecular weight of 320,000 as well as for nonfractionated polydisperse product the adhesion at elevated contact temperatures decreases with increasing polarity of the polymer. The presence of a maximum for both curves does not contradict what was said before, because at the temperature 150° C for SKN-18 and SKN-26 the peeling strength of the bonded specimens is determined by the cohesive strength of the polymer. That, of course, will be higher in the case of a copolymer with a greater content of the polar component. The identical shape of curves *2* and *2* (Figures 4 and 5b) can be explained by the fact that at the high contact temperature the diffusion ability of the molecular chains or of their segments has a comparatively small dependence related to the molecular weight and it is determined primarily by the interaction between polar groups.

Adhesion of butadiene-acrylonitrile copolymers to a nonpolar substrate (polyisobutylene).—The previous experiments showed that adhesion of nitrile copolymers to a nonpolar substrate—PIB, is slightly dependent upon the molecular weight of rubbers. Therefore, only the first and the last fractions of rubber, that is fractions with maximum and minimum molecular weights for the given copolymer, were taken for these experiments.

As one can see from the data of Table 2 the adhesion of polar rubbers to nonpolar substrate is very low and no degree of dependence could be assigned to the changes of polarity of the adhesive, of its molecular weight and of the contact temperature. Such a phenomenon can be explained by the noncompatability of polar nitrile rubbers with nonpolar PIB. This results in the impossibility of diffusion of molecules of the adhesive into the substrate. In this case abrupt difference in the polarity of the adhesive and substrate indicates that even such an intensive factor of the diffusion-acceleration of macromolecules as temperature cannot increase adhesion.

CONCLUSIONS

1. The adhesion of fractions of NBR of varying polarity to a polyamide has been investigated at room and elevated contact temperatures.

2. The adhesion of each copolymer investigated has been shown to fall with the increase of molecular weight of fractions up to a certain limit (300,000–350,000). Above this weight the magnitude of adhesion remains practically constant.

3. The adhesion of all fractions tested increases with increasing contact temperature, attaining the cohesive strength of the respective fraction. The lower the value of molecular weight, the lower is this temperature limit.

4. It was shown that at room contact temperature adhesion of nitrile copolymers to polyamide depends only slightly on the polarity of the adhesive. The lower the polarity of the copolymers, the more the heating of the bonded specimens increases the adhesion strength. The lower adhesion of the polar nitrile copolymers to the highly polar polyamide might be explained by a purely kinetic factor, that is, the lack of flexibility of macromolecules of such polymers and the greater number of intermolecular links, which makes diffusion difficult.

5. It has been established that for bonding at room temperature the adhesion of unfractionated commercial nitrile rubbers to polyamide is determined primarily by the polydispersity of the rubber rather than by its polarity. The adhesion of copolymers at elevated temperatures depends to a high degree on their polarity.

6. It was found that the adhesion of fractions of NBR to nonpolar substrates (PIB) is very low and is independent of polarity and molecular weight, and of temperature of thermal treatment. Smaller values of adhesion in this case are determined by noncompatability of polar adhesive with nonpolar substrates.

7. The results of the work were discussed in the light of the diffusion theory of adhesion.

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RESPONSE OF ELASTOMERS TO HIGH TEMPERATURE CURE*

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It is well known to production people and to process engineers engaged in manufacturing rubber products that the output of curing operations can be greatly increased by elevating the temperature of vulcanization. For example, work done in the 1920's led to the curing of rubber-covered wire at 400° F using a continuous vulcanization (CV) process[1]. Highly accelerated compounds capable of complete vulcanization in 15 seconds at 400° F are used in the wire industry.

More recently the application of high temperature vulcanization methods has been vigorously pressed in the tire industry. While exact curing cycles are closely guarded secrets, it can be stated that passenger tires are vulcanized at temperatures up to 388° F (200 psi steam pressure) using press cycles of the order of 15 to 25 minutes' duration. New automatic presses which shape and then cure the tires at high temperatures—for example, Bagomatic tire curing press, McNeil Machinery & Engineering Co., Akron, Ohio—permit large economies in labor and productivity. Further reductions in curing cycles are anticipated, since the process engineers and rubber technologists continue to develop improved methods of high temperature curing. At this time it appears that the trend to higher temperature vulcanization will not only continue but tend to expand into other lines of rubber products.

Considering the economic advantages which a given company may gain by a major advance in high temperature curing of tires or other rubber goods, it is not surprising that there have been only a few disclosures on high temperature curing technology.

Gray has published on the process of curing wire at 400° F.[1] Juve and Garvey[2] as well as Svetlik and Railsback[3] have reported data on the vulcanizing characteristics of SBR compounds in the temperature range of 250° to 350° F. These authors found that the physical properties of SBR compounds are affected by curing temperature. Brooks, Tronson, and Rowley[4] have reported on the efficiency of certain accelerators in the 400° F curing of wire insulation compounds. In view of the widespread use of high temperature curing, there appears to be a great need for pertinent data illustrating the effect of high temperature vulcanization on the quality of rubber products.

This paper reports additional information which will be of assistance to rubber technologists in selecting and compounding polymers for high temperature curing applications. The work illustrates certain characteristic differences between polymers and between curing systems which have been differentiated in preliminary work in this laboratory. Relatively simple tire compounds were employed in this investigation, and only a few basic physical

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properties were measured. Nevertheless, certain fundamental trends were found.

High temperature vulcanization in the context of this report signifies the curing of compounded rubbers in the range of 350° to 500° F. By way of contrast, the standard or normal temperature of vulcanization is arbitrarily set at 292° F.

METHOD AND RESULTS

Typical tread and carcass compounds were vulcanized at temperatures in the range of 292° to 500° F. The vulcanizates were cured in a steam-heated platen press for temperatures up to 350° F. For cures at temperatures above 350° F an electrically heated two-platen press was used. The preparation of samples, curing, and testing were all done in accordance with the recommendations of ASTM D 1557T. Pnysical properties tested included stress at 300%, tensile strength, and elongation at rupture. Sulfur analyses were also run in certain of the tests in an attempt to characterize the role of sulfur in the mechanism of vulcanization at high temperatures.

Elastomers studied include NR (smoked sheet rubber), SBR (styrene-butadiene rubber), mixtures of NR and SBR, Butyl 215, NBR (paracril), and polychloroprene (neoprene). Contrasts in the response of these compounded elastomers to high temperature vulcanization were studied in terms of the physical properties listed above. A number of curing systems were investigated.

Time-temperature relationships in vulcanization.—Conant, Svetlick, and Juve[5] in a special ASTM task force report summarized factors affecting the problem of obtaining equivalent cures in specimens of various shapes. These authors have developed a nomograph which permits the estimation of lag time or incubation time for curing rubber articles of varying shapes and compositions. This nomograph shows that thermal diffusivity or heat conductance of the rubber compound is very important. Thermal diffusivity controls the rate of conductance of temperature through the article. Values for thermal diffusivities (in inches^2/minute) are shown[5] all of which are low—e.g., from 0.0015 to 0.0131 for hevea tread. It is stated that thermal diffusivity values increase with increased pigment loading and decrease with increasing temperature. Their work covers the temperature range 220° to 340° F.

In transposing from one cure temperature to another, the process engineers often use charts detailing time-temperature relations based on a temperature factor such as 18° F for doubling the cure rate. Such factors are derived from experience with specific compounds and curing processes so they may not be generally applicable to all compounds and all curing processes. Charts applying to the cure range of 350° to 500° F have not yet been developed as far as can be determined by the writer.

In the absence of any guideposts, it was decided to investigate the possibility of obtaining equivalent cures over the temperature range 292° to 500° F. An equivalent cure series was calculated for a number of temperatures in this range based on a doubling factor of 2.0 × for each increment of 18.5° F. This series was vulcanized, and it was soon evident that technical difficulties in manipulating the molding operation made it unlikely that precise control of curing could be exercised with our equipment for cures less than 30 seconds. It became evident too that contrary to conditions prevailing at more normal curing times and temperatures, the factor of thermal diffiusivity produced a large lag in heat transfer in ASTM test sheets. The magnitude of this effect

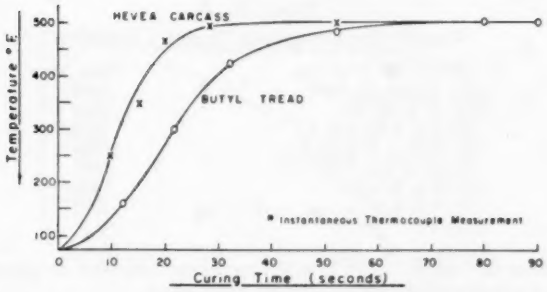

FIG. 1.—Temperature rise in ASTM tensile slabs during 500° F vulcanization.

was measured at 500° F using an instantaneous thermocouple recording instrument for several compounds. The thermocouple (0.012″ gage wire) was placed between two 0.038-inch sheets of the test compound, firmly adhered together, and cured. The curves for the temperature rise during 500° F vulcanization of a natural rubber carcass compound and a butyl tread compound are shown in Figure 1.

These curves demonstrate that mold lag is significant in curing ASTM slabs at 500° F. It appears that it will be extremely difficult to obtain a uniformly cured vulcanizate (at optimum cure) in this range of temperature except in thin test specimens. At normal curing temperatures (and times), mold lag is generally considered to be negligible in ASTM slabs[5]. At 500° F where cures as low as 10 to 30 seconds may be considered feasible, the occurrence of mold lag cannot be overlooked. It would appear then that one of the desirable compound characteristics for high temperature vulcanization would be resistance to overcure or reversion, since the vulcanizate surface would undoubtedly be subjected to overcure before the interior reached optimum cure.

Subsequent work was planned with these practical limitations in mind:

TABLE I

COMPOUNDS STUDIED

Compound	Passenger tread 1	Passenger carcass 2
#1X smoked sheets	—	50.00
SBR 1711	68.75	—
SBR 1551	—	50.00
SBR 1500	50.00	—
Naugatuck #682 reclaim	—	30.00
HAF black	25.00	—
ISAF black	30.00	—
FEF black	—	35.00
Stearic acid	1.00	1.50
Paraflux	3.00	3.00
Flexamine	1.00	—
Naugawhite	—	1.00
XX268 zinc oxide	3.00	4.00
MBT	0.70	0.60
DPG	0.50	0.25
Sulfur	2.00	3.50

TABLE II

CURING CONDITIONS FOR SERIES 1 TESTS

Time of slab cures, min.	Temp, ° F
(1) 15, 30, 45, 90	292
(2) 4, 8, 12, 24	337
(3) 1.5, 2.25, 4.5, 8	365
(4) 0.75, 1.5, 2.25, 4.5	388
(5) 0.75, 1.5, 2.25, 4.5	400
(6) 0.5, 1, 1.5, 3	450
(7) 0.5, 1, 2	500

press operation and mold lag. The curing cycles selected and reported here are not to be considered as an equivalent cure series.

Series 1. High temperature cure of passenger tire compounds, SBR tread and hevea-SBR reclaim carcass.—Typical passenger tire compounds were selected for study in Series 1. These compounds are illustrated in Table I. The SBR tread is based on a blend of SBR 1500 and SBR 1711 while the carcass compound contains a blend of hevea and SBR 1500 as the matrix and is extended with whole tire reclaim.

The curing conditions selected for the Series 1 tests are illustrated in Table II.

The individual values for the several physical properties at each cure level were averaged together to obtain a single index number for simplification of the data presentation. The validity of this method is considered satisfactory for polymers and polymer-curing agent combinations which do not revert. It is probably not as satisfactory for polymers and combinations of polymer and curing agents which do revert, since there would be a relatively greater chance of mixing the optimum cure on slab cures at extremely high temperatures. However, practically, it would appear that within these limitations the methods used in this report would lead to valid conclusions as to the relative effects of high temperature vulcanization on the materials considered herein.

Figure 2 shows the effect of curing temperatures in the range of 292° to 500° F on stress at 300%. The SBR passenger tread compound is shown to retain approximately the same average level of 300% stress values to 400° F curing temperature. The values for 300% stress at 450° and 500° F cure temperatures show some variation possibly due to experimental error, or it may reflect an abnormality in the crosslinking process. In general, however, the

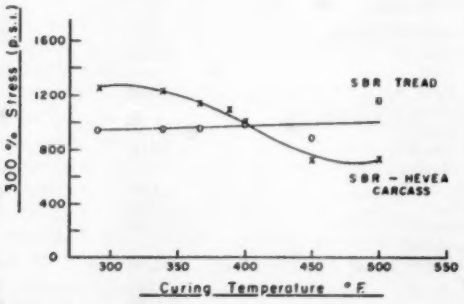

FIG. 2.—Effect of curing temperature on the stress at 300% of passenger tire compounds.

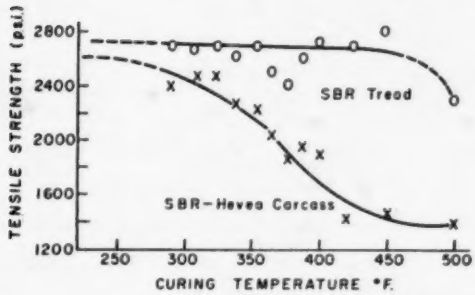

FIG. 3.—Effect of curing temperature on tensile strength of passenger tire compounds.

300% stress level appears to be relatively stable for the SBR tread over this range of curing temperature.

In contrast, the curve for the heavea-SBR compound shows that the higher temperatures of vulcanization exert a relatively deleterious effect on the 300% stress levels of this carcass stock.

Figure 3 illustrates the effect of high temperatures of vulcanization on the tensile strength of these two compounds. The values for the SBR passenger tread show little, if any, effect up to the 450° F curing temperature; and even at 500° F there is only a small drop. In marked contrast the tensile curve of the rubber-SBR passenger tire carcass compound indicates that an increase in curing temperature exerts a deleterious effect on tensile properties. This effect is particularly noticeable at vulcanizing temperatures in excess of 350° F.

The effect of the higher vulcanizing temperatures on elongation at rupture is demonstrated in Figure 4. Interestingly, there is little, if any, appreciable effect noted here. The averaged values for elongation at rupture are substantially unchanged over the entire range of curing temperatures studied.

Effect of cure temperature on sulfur combination.—The Series 1 compounds and cures were studied by means of several sulfur analysis methods to determine the effect, if any, of the increased vulcanizing temperatures on the nature of the sulfur-rubber cross link.

In sulfur-vulcanized rubber the sulfur may be present in several forms, depending on the compound, nature of the curing system, and the physical

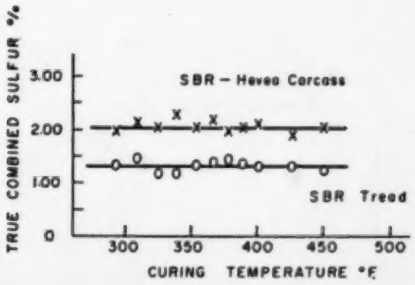

FIG. 4.—Effect of curing temperature on the elongation of passenger tire compounds.

TABLE III

ANALYSIS OF SULFUR IN RUBBER VULCANIZATES

1. Free sulfur	a. Sodium sulfite digestion b. React excess sulfite with formaldehyde c. Titrate sodium thiosulfate iodometrically
2. Total sulfur	a. Digest in brominated nitric acid b. Perchloric acid oxidation c. Barium sulfate precipitation
3. Sulfide sulfur	a. Digest in acetic-hydrochloric acids mixture b. Absorb H_2S in ammoniacal zinc solution c. Acidify and titrate H_2S with iodine and thiosulfate
4. True combined sulfur	a. Sample from 3-c b. Acetone extraction c. Total sulfur as in 2

factors of vulcanization such as time and temperature. In this work the Series 1 vulcanizates were analyzed for these forms of sulfur:

1. Free (uncombined) sulfur
2. Sulfide sulfur
3. True combined sulfur

The true combined sulfur is considered to be sulfur actually combined with the rubber molecules in the form of cross links or in the hydrocarbon chain. True combined sulfur is defined as nonextractable sulfur which remains in the vulcanizate after both the free sulfur and the sulfide sulfur have been extracted.

Table III shows a brief outline of the methods used in these separate sulfur analyses[6].

Figure 5 shows the effect of increased vulcanizing temperatures on the true combined sulfur levels of the Series 1 tread and carcass compounds. The plot is seen as a linear function up to 450° F. No test was made of the 500° F cures. The data demonstrate that on the average the proportion of sulfur which crosslinks with polymer, at least in these two typical passenger tire compounds, is similar at all curing temperatures tested.

In contrast the sulfide sulfur level tends to increase with increase in curing temperature. Figure 6 demonstrates that the average sulfide sulfur level increases with increase in vulcanizing temperature. This trend is particularly noted in the case of the carcass compound which contains a blend of hevea and

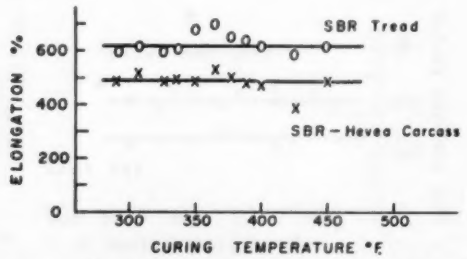

FIG. 5.—Effect of curing temperature on true combined sulfur.

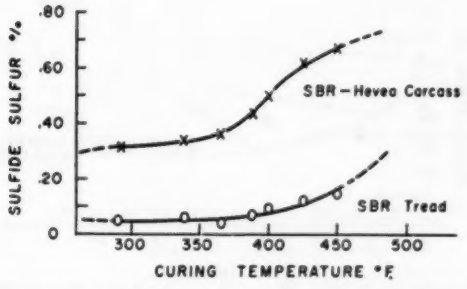

FIG. 6.—Effect of curing temperature on sulfide sulfur formation.

SBR as the polymeric matrix. The slope of the sulfide sulfur curve for the carcass compound shows a sharp inflection at about 360° F curing temperature. The rise in sulfide sulfur for the SBR tread is much less pronounced than for the carcass compound. It is considered that a rise in sulfide sulfur may be associated with reversion of the rubber during cure. In Figure 7 the relationship between tensile strength and sulfide sulfur is demonstrated for these two Series 1 compounds. An approximately linear relationship is shown for both compounds relating sulfide sulfur to tensile strength. The cure temperatures are not indicated in this graph. However, the points, from left to right, represent sequentially the successive increments of cure temperatures tested and shown in Table II. It is seen that in the case of the rubber-SBR carcass the formation of sulfide sulfur is associated with overcure and reversion of the rubber component of the carcass compound. Little or no effect is noted for the SBR tread.

Sulfide sulfur may be formed from the residue of free sulfur in the later phases of cure. Figure 8 details the relation of free sulfur to sulfide sulfur for the rubber-SBR carcass compound. It is noted that the highest levels of sulfide sulfur are associated with the lowest levels of free sulfur. Very low values of free sulfur are indicative of overcure and may be associated with reversion in the case of natural rubber compounds. In contrast SBR is essentially nonreverting, so it would not be expected that this relation would be found for the passenger tread.

The Series 1 results show the quality of the SBR tread, as judged by laboratory tests, to be largely unaffected by high temperature vulcanization, while the

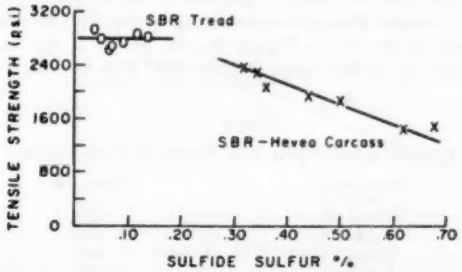

FIG. 7.—Relation of sulfide sulfur to tensile strength of passenger tire compounds.

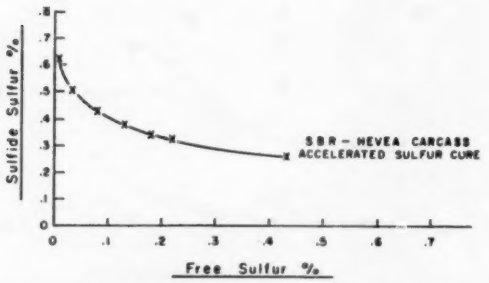

FIG. 8.—Relation of sulfide sulfur to free sulfur in passenger tire carcass compound.

same curing conditions are shown to produce a deleterious effect on the quality of the hevea-SBR carcass compound.

It was suspected that the decreased quality of the carcass stock under high temperature vulcanization might be associated with the natural rubber component of the carcass compound. Therefore, Series 2 was initiated to isolate the effect of rubber per se in carcass compounds during high temperature cures.

TABLE IV

SERIES 2 CARCASS COMPOUNDS

Compound	3	4	5
Polymer type	SBR	SBR-Hevea blend	Hevea
SBR 1500	100	50	—
#1X smoked sheets	—	50	100
Naugatuck #682 reclaim	30	30	—
Stearic acid	1.5	1.5	3
Paraflux	3.0	3.0	—
FEF black	35	35	35
BLE 25	1.0	1.0	1.5
Pine tar	—	—	5.0
MBTS	0.80	0.70	0.70
DPG	0.60	0.35	—
Sulfur	3.50	3.50	3.50
ZnO	3.0	3.0	3.0

Series 2. SBR and hevea carcass compounds.—Table IV illustrates the carcass compounds used for the Series 2 portion of the study.

The effect of increased curing temperatures on the 300% stress of these three carcass compounds is shown in Figure 9. In Series 2 the compounds were cured in 50° increments in the range 292° to 500° F as is shown in Table V.

TABLE V

CURING CONDITIONS FOR SERIES 2 COMPOUNDS

Times, min.	Temp, ° F
45 and 90	292
4 and 8	350
2 and 4	400
1 and 2	450
½ and 1	500

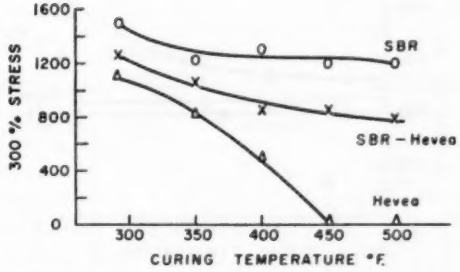

FIG. 9.—Effect of curing temperature on the stress at 300% of tire carcass compounds.

As in Series 1, the data of Series 2 at each curing temperature were averaged for presentation in this report.

The curves of Figure 9 demonstrate that sulfur-cured hevea rubber is indeed highly sensitive to the higher vulcanizing temperatures. The 300% stress values decrease steadily with increasing curing temperature until at 450° F virtually no cure at all is obtained. In many replicate tests at 450° F or higher, sulfur-cured hevea rubber vulcanizates always have shown a badly degraded tacky surface with sponginess in the interior of press cured slabs. In contrast the SBR carcass compound of Figure 9 shows little, if any, effect on 300% stress as the curing temperatures are increased. Compound 4, containing a blend of hevea and SBR, shows an expected intermediate level of 300% stress values. The curve for compound 4 demonstrates a decrease in stress but lies intermediate between the curves for the SBR and hevea compounds.

Figure 10 presents data illustrating the effect of the higher vulcanizing temperatures on the tensile strength of the Series 2 carcass compounds. The SBR carcass (compound 3, Table IV) shows only a small effect. In contrast, the deleterious effect of the higher temperatures on the tensile strength values of hevea rubber (compound 5, Table IV) is clearly demonstrated.

The hevea carcass (compound 5) cured at 292° F shows much higher tensile strength than the SBR compound (compound 3). With increase of curing temperature the hevea vulcanizates are subject to a loss of tensile strength. The curve for the hevea carcass intersects that for the SBR carcass at about 385° F. The curve for the hevea-SBR compound (compound 4) is intermediate,

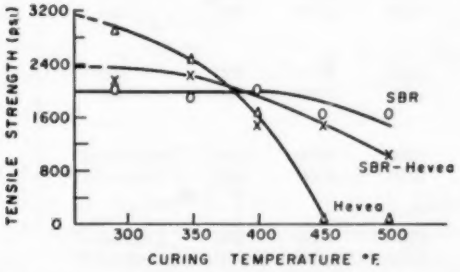

FIG. 10.—Effect of curing temperature on the tensile strength of tire carcass compounds.

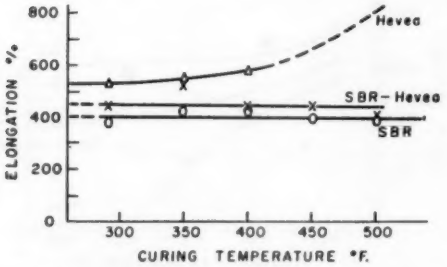

FIG. 11.—Effect of curing temperature on the elongation of tire carcass compounds.

and it reflects the deleterious effect of the higher curing temperatures on the natural rubber component of the blend.

Figure 11 illustrates the averaged values for elongation at rupture obtained at the various levels of cure temperatures tested. Both compounds 3 and 4 are largely unaffected, as shown in the two lower plots. However, the upper curve, for the hevea carcass, shows an inflection in the direction of higher elongations which would normally be associated with reversion of cure.

The Series 2 tests demonstrate a fundamental difference between hevea rubber and SBR in response to the higher temperatures of vulcanization in sulfur-cured vulcanizates. The curing conditions used in this work in the range 400° to 500° F apparently cause an overcure or reversion of natural rubber. Practically, however, the tendency to overcure or reversion for a

TABLE VI

CONTRASTS BETWEEN SBR AND HEVEA IN HIGH TEMPERATURE CURING

	SBR			Hevea		
Polymer	Stress at 300%, psi	Tensile, psi	% elongation at rupture	Stress at 300%, psi	Tensile, psi	% elongation at rupture
Cured at 292° F						
45 min	1500	2030	400	1170	2930	530
90 min	1550	2030	370	1070	2930	530
Cured at 350° F						
4 min	1140	1930	450	900	2670	550
8 min	1330	1870	400	800	2330	550
Cured at 400° F						
2 min	1340	1870	400	500	1580	560
4 min	1300	2190	450	500	1750	600
Cured at 450° F						
1 min	1200	1630	400	Degraded*	—	—
2 min	1210	1660	400	Degraded*	—	—
Cured at 500° F						
½ min	1200	1650	400	Degraded*	—	—
1 min	1220	1620	390	Degraded*	—	—

* Surface became tacky; interior of vulcanizate was spongy.

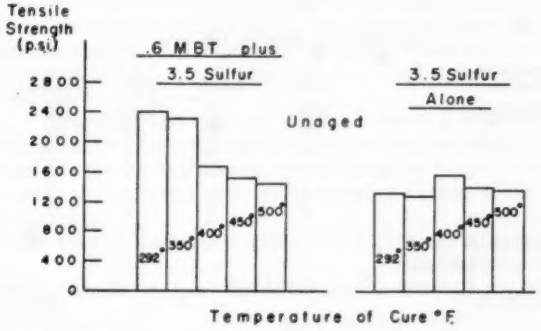

FIG. 12.—Effect of curing temperature on the tensile strength of passenger tire carcass compounds.

given polymer would possibly be recognized as a polymer deficiency for applications in high temperature vulcanization.

Contrasting effects of high temperature vulcanization.—More detailed data are shown below (Table VI) illustrating some of the problems involved in judging the effects of high temperature curing. Table VI shows that the curing conditions selected produced a reasonable degree of cure for the SBR (compound 3), although tensile decreased with increase in curing temperature. The stress at 300% values were equivalent for all cures except those at 292° F. In contrast, the 300% stress values and tensile results for the natural rubber compound were drastically reduced with increase of cure temperature. Natural rubber reverts on overcure, and it is possible that optimum cure would be passed within a few seconds at 500° F curing temperature.

Series 3. Sulfur accelerator versus sulfur alone.—It was considered as one facet of the general industry advance in curing temperatures that it might become possible to eliminate accelerators using sulfur as the sole curing agent. Series 3 features a comparison of sulfur-accelerator versus sulfur alone in the rubber-SBR tire carcass compound 2. In this instance MBT was used as the sole accelerator; no DPG was used.

Figure 12 shows the averaged tensile strength at the several curing levels selected. The curing conditions were similar to those shown in Table V for the

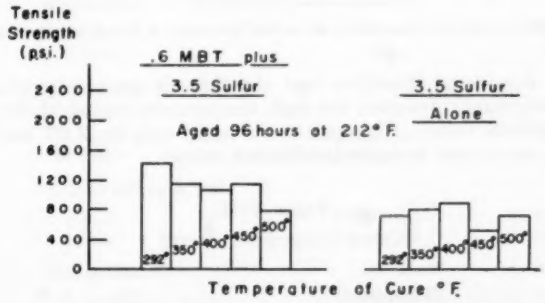

FIG. 13.—Effect of curing temperature on the tensile strength of passenger tire carcass compounds.

TABLE VII

RECIPES FOR SERIES 4 COMPOUNDS

Compound Curing agent	6 Sulfur	7 Resin[a]	8 YDO	9 Peroxide	10 GMF
#1X smoked sheets	100	100	100	100	100
FEF black	40	40	40	40	40
#8 oil	4	4	4	4	4
Laurex	3	3	3	3	3
BLE 25	1.5	—	—	1.5	1.5
Zinc oxide	2	2	2	2	2
Resole resin[a,b]	—	10	—	—	—
YDO (2,2'-methylene-bis-(4-chloro-6 methylolphenol))	—	—	6	—	—
MBTS	0.5	—	—	—	2.0
Dicumyl peroxide 90%	—	—	—	5.0	—
Sulfur	3.0	—	—	—	—
Stannous chloride dihydrate	—	2	—	—	—
GMF	—	—	—	—	3.0

[a] Resin cure[7].
[b] Commercial *tert*-butylphenyl resole resin.

Series 2 work. Figure 12 illustrates that at temperatures of 400° F or above there is no essential difference in tensile strength between accelerated or unaccelerated sulfur-cured tire carcass compounds. In contrast, the data of Figure 13 show that the MBT accelerated compound resists heat aging much better than the compound vulcanized with sulfur alone at all levels of curing tempera-

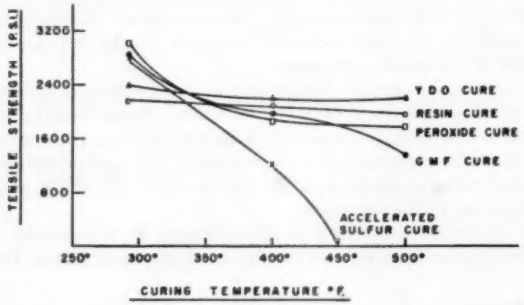

FIG. 14.—Effect of type of curing system on the tensile strength of Hevea carcass compounds.

ture. It is considered therefore that the thiazole accelerator should be included in compounds designed for high temperature curing at the very least for its antioxidant value. This rule would apply only to MBT and its derivatives, which are known to exert antioxidant value[8].

TABLE VIII

CURING CONDITIONS, SERIES 4

Times, min.	Temp, ° F
45 and 90	292
2 and 4	400
½ and 1	500

It is well known that in curing thick rubber products a temperature gradient exists due to slow thermal diffusivity[5]. It is believed that this fact would in itself necessitate the use of accelerators, especially under extreme conditions of vulcanization such as 500° F where the time lag factor in heat transfer would be very large on short cure cycles.

Series 4. Nonsulfur vulcanization of hevea.—Series 2 showed high temperature vulcanization to produce an extremely deleterious effect on sulfur-cured hevea. Various other curing systems were therefore examined to determine if this effect might be a polymer response or merely a characteristic specific to the sulfur-curing system.

The recipes for the compounds evaluated in Series 4 are illustrated in Table VII.

The curing conditions used for the work in Series 4 are summarized in Table VIII.

TABLE IX

PHYSICAL PROPERTIES OF SERIES 5 COMPOUNDS

	MBTS plus Sulfur	Accelerators Only
Press cured at 292° F		
M-300, psi		
45 min	1590	1800
90 min	1390	1860
Tensile strength, psi		
45 min	3700	3410
90 min	3240	3280
Elongation, %		
45 min	550	480
90 min	530	450
Press cured at 400° F		
M-300, psi		
2 min	710	1400
4 min	590	1250
Tensile strength, psi		
2 min	1880	2580
4 min	1580	2680
Elongation, %		
2 min	530	450
4 min	550	450
Press cured at 500° F		
M-300, psi		
½ min	Degraded	770
1 min	Degraded	600
Tensile strength, psi		
½ min	Degraded	1480
1 min	Degraded	1190
Elongation, %		
½ min	Degraded	450
1 min	Degraded	450

TABLE X

RECIPES FOR SERIES 6 TESTS

Compound	Butyl 13	Butyl 14	Paracril BLT 15	Neoprene W 16
GRI 215	100	100	—	—
Paracril BLT	—	—	100	—
Neoprene W	—	—	—	100
Spheron 6	50	50	50	40
Resole resin[a]	9[b]	—	—	—
Stannous chloride dihydrate	1.5	—	—	—
YDO	—	5[c]	—	—
Circo light oil	—	3.75	5	5
Stearic acid	—	—	—	—
Laurex	—	1.25	—	—
Zinc oxide	—	—	5.0	4.0
XLC magnesium oxide	—	—	—	3.0
MBTS	—	—	0.70	—
Monex (TMTM)	—	—	0.25	—
Sulfur	—	—	1.5	0.75

[a] Commercial *tert*-butylphenyl resole resin.
[b] 1.0 part resin added to polymer and black as a promoter during hot processing in Banbury.
[c] 1.0 part YDO used similarly in this stock.

As in the previous comparisons, the physical properties data were averaged for each temperature of cure.

Figure 14 shows that a fundamental difference exists in the vulcanizing behavior of natural rubber using the several different curing systems. This graph demonstrates that in contrast to the accelerated sulfur-cured system, resin-cured hevea, YDO (a polymethylol phenol)-cured hevea, peroxide-cured hevea, and GMF-cured hevea are all relatively stable when press-cured at temperatures up to 500° F.

The resin used in this work is a commercial-resole resin (*tert*-octylphenyl). YDO is 2,2′-methylene-bis-(4-chloro-6-methylolphenol). This latter curing agent is considered to be an improvement on the stannous chloride-activated resole resin-curing combination, since YDO contains its own built-in chlorine activator.

These compounds were not adjusted to either equal modulus or to equal hardness. It would be possible so to adjust these compounds except for the sulfur-cured compound which reverts.

Series 5. Use of sulfur-bearing accelerators in hevea.—The Series 4 tests showed the previously noted instability of natural rubber at high temperatures of vulcanization to be related to the use of the sulfur curing system. Just what the role of sulfur might be in the deterioration of physical properties during high temperature cures is not known. A comparison of sulfur cure with sulfur-bearing accelerators was made to throw some light on this subject. The sulfur-cured carcass of Series 4 was therefore compared under the Series 4 test conditions with a similar compound containing sulfur-bearing accelerators but no elemental sulfur. The compound features are shown below:

Compound	11	12
Sulfur	3.0	—
MBTS	0.50	—
Dibutyl xanthogen disulfide	—	3.0
Zinc dibutyldithiocarbamate	—	3.0

TABLE XI

CURING DATA FOR SERIES 5

Cure, °F	Curing agent Time, minutes	Butyl resin	Butyl YDO	Paracril BLT sulfur	Neoprene W, metallic oxide
		Average tensile, psi, Elongation, %			
		Unaged			
292	45 and 90	2075–615	1635–490	4000–550	2440–480
350	4 and 8	1870–615	1540–520	3350–580	2850–460
400	2 and 4	2100–560	1920–455	3600–595	2630–260
450	1 and 2	2150–545	1890–420	3060–520	2440–235
500	½ and 1	1825–460	2025–420	2925–500	1985–200

The results obtained are shown in Table IX. At the higher curing temperatures, the combination of sulfur-bearing accelerators produced a relatively stable system compared to the control cured with elementary sulfur and MBTS. It is suggested that elemental sulfur may promote deterioration of hevea at the elevated curing temperatures.

Series 6. Butyl, neoprene, and paracril polymers.—Tests were run in Series 6 to evaluate the response of elastomers other than hevea and SBR to the higher curing temperatures. The recipes used in the Series 6 tests are shown in Table X.

The physical properties obtained on vulcanizates of these compounds are shown in Table XI.

These data indicate that both resin-cured butyl and YDO-cured butyl show relatively flat curing characteristics over the range of curing temperatures studied (292° to 500° F). Paracril BLT cured with sulfur shows the same good stability to high curing temperatures found in SBR but with inherently higher tensile properties. Neoprene W in this test showed a lack of stability to high

TABLE XII

RECIPES FOR SERIES 5-A TESTS

Compounds	17	18	19
Curing agent	Butyl tread sulfur	Butyl tread resin	Neoprene tread metallic oxides
Butyl 215	100	100	—
Neoprene GRT	—	—	100
MPC black	50	50	—
HAF black	—	—	27.5
Petroleum oil	5	5	—
Zinc oxide	3	—	5
XLC magnesia	—	—	4
#8 oil	—	—	7
Microcrystalline wax	—	—	3
MBTS	1	—	0.38
Tuex	1.25	—	—
Resole resin[a]	—	8.0	—
Stearic acid	1	—	—
Sulfur	0.75	—	—
BLE-25	1	—	1.0
Flexamine	1	—	—
Stannous chloride dihydrate	—	1.6	—

[a] *Tert*-octylphenyl resole resin.

TABLE XIII

CURING DATA FOR SERIES 5-A

Cure, °F	Polymer curing agent: Time, minutes	Butyl sulfur	Butyl resin	Neoprene metallic oxides
		Average tensile, psi, average elongation, %		
		Unaged		
292	45 and 90	2595–685	1695–675	3730–650
400	4 and 8	2330–765	1480–625	3270–535
500	2 and 4	70–800+	1465–555	2630–415
500	6 and 10	Degraded	1420–640	2040–270

temperature curing, as evidenced by low values for elongation at rupture in the samples cured above 350° F.

Further work was done with Neoprene GRT and with Butyl 215. The recipes used in this latter work are illustrated in Table XII.

Results obtained at several curing levels on the compounds of Table XII are shown in Table XIII.

The results shown in Table XIII indicate that the resin-cured butyl is stable under high temperature vulcanizing conditions. In contrast, sulfur-cured butyl is reverted badly at temperatures in excess of 400° F. Neoprene GRT, cured with metallic oxides, is shown to be unstable at the highest curing temperatures.

Figure 15 contrasts the effect of curing temperature on the average tensile properties of the polymers evaluated in Series 5 and 5-A.

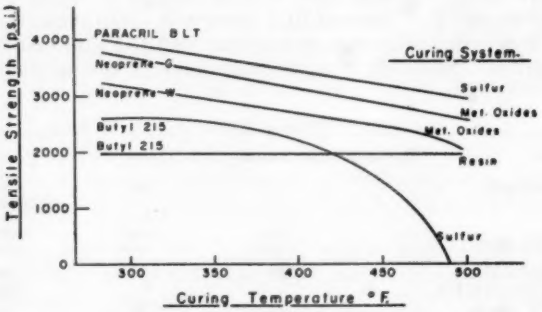

FIG. 15.—Effect of curing temperature on tensile strength of the tread compounds of several polymers.

DISCUSSION OF RESULTS

Within the curing range studied (292° to 500° F), an increase in the vulcanization temperature exerted a deleterious effect on all polymers. The effect is most marked above 370° F. However, the magnitude of the effect varies for each elastomer and can be inhibited or largely prevented by choosing the proper curing system for polymers like rubber and butyl which revert to the higher temperatures.

Sulfur-cured vulcanizates of natural rubber revert badly above 360° to 370° F. The synthetics SBR and NBR show significantly superior stability compared to hevea at elevated curing temperatures. In these tests polychloro-

prene showed marked instability but is shown to be more stable than sulfur-cured hevea.

Butyl vulcanizates cured with stannous chloride activated resole resins or with YDO [2,2′-methylene-bis-(4-chloro-6-methylolphenol)] show flat curing characteristics up to 500° F. Sulfur-cured butyl is shown to revert badly in the range 400° to 500° F.

These tests illustrate that selection of the proper curing system extends the curing range of Hevea and butyl. Resin curing systems and YDO are quite effective with these polymers and may be applicable to all polymers. The peroxide cure and the GMF cure may also be applicable.

For the future a continuance of the trend to automation and higher curing temperatures seems indicated. The present results suggest that compounders should carefully examine their choice of polymer and curing system for high temperature curing applications.

In sulfur-cured products SBR may be chosen because of its relative stability in high temperature cures. On the other hand resin-cured butyl or YDO-cured butyl may permit 500° F cures and extremely short press cycles so as to be preferable in many rubber products.

One of the admitted deficiencies of butyl is its relatively low thermal diffusivity (0.0053–0.0083)[5] resulting in decidedly longer cure times for products like tires (35- to 40-minute cure cycle recommended)[9]. It is suggested that butyl tires cured with the resin or with YDO might be processed at much higher temperatures of vulcanization than is now possible with sulfur-cured butyl tires.

The relative stability of Paracril NBR is of interest where high temperature curing is desired for increased productivity in oil-resistant products.

Lastly, it has been demonstrated that natural rubber may be useful in certain high temperature curing applications, provided that adequate stability is built into the compound by selecting a stable curing system.

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THE INTERACTION OF CARBON BLACK WITH SULFUR, MBT AND TMTD IN VULCANIZATION *

G. A. Blokh and Ch. L. Melamed

The value of carbon black as a reinforcing agent in the production of vulcanized rubber is well-known[1]. Nevertheless until recently, usually the mechanism of the reinforcement has been investigated from the physical aspect[2–6]. More recent investigations of the structure and composition of carbon blacks[7,8] have made it possible to interpret the mechanism of reinforcement of rubber by carbon blacks not only from the physical but also the chemical viewpoint.

It has been established[9] that the structure of carbon black contains functional active groups—OOH, OH, COOH, C=O and so on. The presence of C=C bonds has been noted; these are particularly characteristic of the structure of furnace blacks produced in an atmosphere poor in oxygen. The possibility of the participation of the carbon black in the chemical reactions of vulcanization is indicated also by the unsaturated character of certain grades of carbon black as shown by bromine reaction.

It has been noted[10] that the reaction capacity of carbon blacks, determined by the content of oxygen groups (e.g. quinones) upon the surface of the particles, varies markedly under the influence of heat treatment. It is found that

Table 1

Designation of carbon black	Specific surface, in sq m/g
Channel	93
Furnace	36
Thermal, standard	11
Thermal, high dispersity	29

p-quinone dioxime, *p*-nitrodiphenylamine, hexachlorocyclopentadiene and other compounds are promoters of the reaction of rubber and carbon black, giving rise to alkyl or aryl radicals of rubber which react with the active centers on the surface of carbon black with the formation of covalent bonds.

It is very probable that in the process of vulcanization there takes part interaction of the functional groups of the carbon black with the sulfur and accelerators and then with the rubber with the formation of units of the vulcanization network. As was shown by Lezhnev and Kuz'minskiĭ the antioxidant phenyl-2-naphthyl amine reacts chemically with certain of the active oxygen groups of carbon blacks[16].

It is well-known that certain types of carbon black are characterized by huge surface areas (Table 1).

There is reason to suppose that the huge surface of carbon blacks is the locus for many chemical and exchange reactions developing in the process of vulcanization. It is precisely in the adsorption films of unvulcanized rubber on

* Translated by R. J. Moseley from *Izvest. Vyshikh. Ucheb. Zavedenii Tekhnol. Legkoĭ Prom.* 1939, No. 2, 28–38; a translation of RAPRA of Great Britain, No. 847.

the surface of the carbon black that there take place complex chemical processes of interaction of accelerator-vulcanizing substances both among themselves with the formation of unstable polysulfides and with the molecules of raw rubber and the active centers of carbon black with the formation of a single spatial network, on account of the interaction of raw rubber with sulfur, accelerators and carbon black.

In order to test these ideas experimentally it was necessary in the first place to demonstrate experimentally the presence of chemical interaction between the carbon black and sulfur and between the carbon black and the accelerators. It was necessary also to clear up the influence of removal of the hydroxyl groups upon the reinforcing properties of the carbon blacks.

The present investigation was carried out by the radioactive isotope, or tagged atom, method. We studied the interaction of the carbon black (lamp and channel) with S^{35}, radioactive sulfur. For the study of the interaction of carbon black with accelerators we synthesized radioactive mercaptobenzthiazole, MBT, and radioactive tetramethylthiuram disulfide, TMTD.

INTERACTION OF CARBON BLACK WITH SULFUR

We investigated a carbon black-sulfur mixture in which the carbon black-sulfur ratio was 100:3, in the three following variants:

1. Accurate portions of carbon black (channel or lamp) are mixed uniformly with an accurate portion of radioactive sulfur and then heated for 1, 3, 5, 8 and 10 h at 100° and 145° C.
2. Accurate portions of radioactive sulfur are heated under analogous conditions and then mixed with carbon black.
3. Accurate portions of carbon black and radioactive sulfur are mixed together but not subjected to heating (a blank test).

Then from each series of experiments we took portions of a mixture of carbon black with radioactive sulfur for determination of initial radioactivity I_0 in a scintillation counter.

After this the mixes indicated, with various conditions of thermal treatment, were subjected to continuous prolonged extraction with benzene, cold (i.e. without heating), in order to remove free radioactive sulfur. The extraction lasted 600 h. After strictly determined periods of extraction samples of carbon black were taken and the presence of residual radioactivity I_t investigated afresh. Carrying out experiments of variants 2 and 3 made it possible

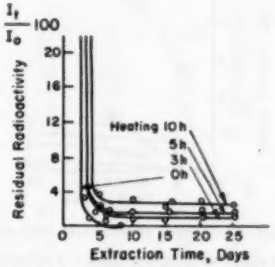


FIG. 1.—Lamp black and radioactive sulfur at 145° C.

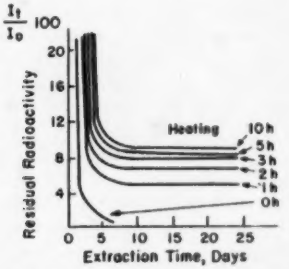


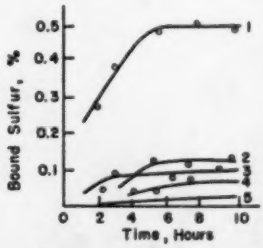
FIG. 2.—Gas black and radioactive sulfur at 145° C.

to explain the qualitative aspect of the adsorption binding of the sulfur with the carbon black. Comparison of the residual radioactivity of the carbon black from experiment 1 with the analogous data of experiments 2 and 3 made it possible to determine the true picture of the chemical binding of the radioactive sulfur with the carbon black.

The kinetic data for the binding of sulfur with gas and lamp black at 145° C, on the basis of comparison of the residual radio-activity with the original radioactivity before the extraction of the sulfur are given in Figures 1 and 2.

An analysis of the data presented makes it quite evident that chemical interaction at 145° takes place between carbon black and the sulfur. Even continuous extraction with benzene of the mixture of sulfur and carbon black, lasting to 600 h, is not enough to separate the sulfur from the carbon black; however we do not find the same state of affairs in the case of a carbon black-sulfur mixture not subjected to heating. Gas (channel) black is, as we might expect, able to react chemically with the sulfur to a considerably greater extent than lamp black (Figure 3).

Our figures lie close to those of Studebaker[11], in whose experiments one part of carbon black was heated with 9 parts of sulfur for 18 h at 150° C. After 28 days extraction with toluene Studebaker established the presence of 0.64% bound sulfur. As may be seen from Figure 3, according to our data 0.5% of the sulfur is bound with channel black. Dogadkin, Lukin et al. reach similar conclusions[12]. These authors note that the chemical activity of channel black increases after hydrogenation. The interaction of carbon black with sulfur



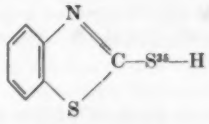
→ Time of heating of carbon black with sulfur.

FIG. 3.—Kinetics of reaction of sulfur with carbon black. *1*—Gas black and S^{35} heated at 150°; *2*—S^{35} heated at 150° and mixed with gas black; *3*—Lamp black and S^{35} heated at 150°; *4*—S^{35} heated at 150° and mixed with lamp black; *5*—Gas black and sulfur without heating.

leads to an approximately two-fold increase in the dimensions of the carbon black aggregates, determined from the light absorption of suspensions produced by ultrasonic vibrations (of a frequency of 10,000 c/s). From this fact the conclusion is drawn in the paper that the sulfur reacts with carbon black in the form of a biradical capable of binding the separate particles of carbon black with each other or else of binding the sulfhydryl groups formed in the reaction of the sulfur with the functional groups of carbon black and capable of reacting with the active oxygen groups or other groups of other particles of carbon black. In further investigations by Dogadkin, Skorodumova and Kovaleva[18] it was found that sulfur in general reacts with active particles of the surface of carbon black, representing the olefinic double bonds of the surface hexacarbonic groupings in the structure of the carbon black.

INTERACTION OF CARBON BLACK WITH MBT

For the investigation of the interaction with carbon black it was necessary to synthesize tagged MBT. We produced radioactive MBT[13] having the structure:



The portions of carbon black (lamp or channel) and of radioactive MBT mixed in the ratio 100:3 were subjected to preliminary heating at 100 and 145° C from 30 to 300 min. After heating we determined the initial radioactivity of the mixture of carbon black and radioactive Captax (I_0). Then this mixture

TABLE 2

KINETICS OF REACTION OF RADIOACTIVE MBT WITH CARBON BLACK (RESIDUAL RADIOACTIVITY)

$\left(\frac{I_t}{I_0}100\right)$

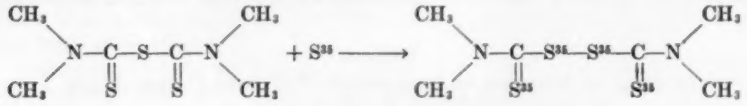
Time of extraction in h	Without heating	Time of heating at 100° C, min				Time of heating at 150° C, min			
		30	60	180	300	30	60	180	300
Gas black									
Before extraction			100						
68	31	93.5	95.7	97	99	84	90	87	76
164	45	83	97	91	96	82	78	76	78
305	32	69	93	93	97	83	91	92	92
409	30.4	68	95	89	76	81	93	84	89
666	32	69	94	91	88	87	—	78	85
Lamp black									
Before extraction			100						
68	39	51	62	69	71	75	82	—	88
164	32	34	60	67	71.6	48	43	51	45
305	28	35	59	77	67.0	51	49	46	41
409	34	41	65	65	73.0	40	41	47	47
666	34	34	52	66	—	42	45	45	48

was subjected to cold extraction with methanol for 666 h with replacement of the methanol by fresh after every 24 h. After definite intervals of time samples of carbon black were taken and the residual radioactivity (I_t) determined.

Comparison of the residual radioactivity with the initial $\left(\frac{I_t}{I_0}100\right)$ makes it possible to decide the presence or absence of interaction of MBT with carbon black. If chemical interaction of the sulfhydryl groups with the active centers of the carbon black takes place the MBT becomes bound and the amount extracted falls with the length of time of extraction and as a function of the time of previous heating. The resulting data, presented in Table 2, show that proportionally to the time of heating of the carbon black with the MBT there takes place chemical interaction between these, and in the case of gas black this interaction is particularly well defined. From a comparison of the activities after extraction of the gas black-MBT mixture (without previous heating) and of an analogous gas black-MBT mixture (with previous heating) it is seen that in the former case there takes place an adsorption of MBT by the carbon black (32 to 34% residual activity in relation to the initial) whereas in the case of heating of carbon black with MBT the residual radioactivity is maintained at a level above 90% in relation to the initial activity, which points to the existence of chemical binding.

INTERACTION OF CARBON BLACK WITH TMTD

Interaction was effected between tetramethylthiuram monosulfide and an equimolecular quantity of radioactive sulfur in an atmosphere of nitrogen at a temperature of 120° C, i.e. the reaction



was carried out.

The liberated radioactive tetramethylthiuram disulfide had a melting point of 143–144° C.

In addition, portions of carbon black and radioactive TMTD, taken in the proportion 100:3, were subjected to heating at 100° and 145° for various periods. After determination of the initial radioactivity (I_0) of the carbon black-

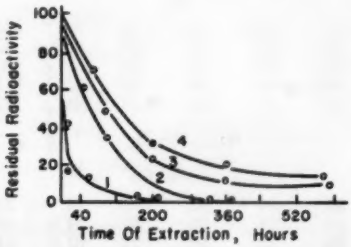


FIG. 4.—Interaction of thiuram with lamp black. *1*—without heating; *2*—heating at 145° for 30 min; *3*—60 min; *4*—180 min.

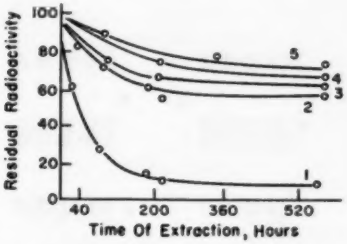


FIG. 5.—Interaction of thiuram with channel black. *1*—without heating; *2*—heating at 145° for 300 min; *3*—30 min; *4*—180 min; *5*—60 min.

TMTD mixtures the latter were subjected to prolonged cold extraction with benzene. As in the case of sulfur or MBT, we determined the residual radioactivity of the carbon black (I_t) after definite intervals of time.

The resulting data are presented in Figures 4 and 5.

Analysis of the curves allows us to conclude that in the process of heating of TMTD with carbon black there takes place decomposition of the TMTD and a chemical interaction of the sulfur containing products of decomposition of the thiuram with the active centers of the carbon black.

In the light of the data obtained by the electron paramagnetic resonance method[14] under the influence of TMTD, there were formed under the temperature conditions of our experiments polymeric radicals which in their turn entered into chemical bonds with the carbon black, sulfur and accelerators, forming crosslink structural units.

INFLUENCE OF HIGH-TEMPERATURE HEATING OF CARBON BLACKS UPON THEIR REINFORCING PROPERTIES

In order to show the influence of removal of active hydroxyl centers from the carbon black structure upon the reinforcing properties of carbon blacks these latter were subjected to high temperature heating to 900 to 1700° C (this was carried out by G. S. Grishko).

Three types of carbon black were subjected to thermal treatment—channel gas, lamp and thermal. Heating was carried out in electric furnaces, in which magnesite tubes were placed, filled with carbon black. The temperature of the electric furnace was observed by means of an optical pyrometer. The heating of the carbon black from 20 up to 900° C lasted 3 h, at 900° 1.5 h (in all 4.5 h); from 20 to 1700° C 4.5 h and at 1700° C 1.5 h (in all 6 h). Then the heat-treated black was compounded, mixed, cured and the cured specimens subjected to physical testing (Table 3).

An analysis of the data makes it possible to draw the following conclusions:

1. Heating of channel black at 1400 to 1700° C leads to a sharp fall in the tensile strength of vulcanizates based on SKS-30. In point of fact the strength properties of vulcanizates with chemical black heated at 1700° and of vulcanizates on non-heated thermal black are on the same level.

2. Heating of thermal black at 900–1400–1700° C had only an insignificant influence upon the physical properties of vulcanizates based on SKS-30 and on chloroprene rubber (Nairit).

3. Heating of lamp black at 900 to 1400° did not lower the physical proper-

TABLE 3

INFLUENCE OF HIGH-TEMPERATURE TREATMENT OF CARBON BLACKS UPON THE STRENGTH PROPERTIES OF THE VULCANIZATES

Cure time at 145° C, min	Without heating[1]			Temperature conditions of heating of carbon blacks in ° C											
				900			1200			1400			1700		
	σ	L	M_{300}	σ	L	M_{300}	σ	L	M_{300}	σ	L	M_{300}	σ	L	M_{300}
							Gas black								
							(SKS-30 rubber)[2]								
10	150	760	55	247	650	33	240	650	49	119	530	46	105	520	47
20	190	620	70	214	560	56	185	560	67	121	550	47	119	510	60
30	168	520	67	215	540	58	159	500	79	114	500	50	93	420	66
60	166	500	66	218	540	61	164	500	80	117	500	50	103	400	57
							Thermal black								
							(SKS-30 rubber)								
10	98	400	68	102	400	70	—	—	—	75	350	69	79	400	51
20	78	380	65	97	370	69	—	—	—	89	420	49	82	400	69
30	97	420	76	100	390	65	—	—	—	78	400	71	78	450	48
60	108	420	80	104	410	64	—	—	—	80	350	75	75	460	59
							Lamp black								
							(SKS-30 rubber)								
10	62	300	37	75	400	45	—	—	—	89	560	44	—	—	—
20	70	370	37	80	430	44	—	—	—	95	580	47	—	—	—
30	75	380	35	84	470	42	—	—	—	104	600	42	—	—	—
60	73	360	34	82	460	40	—	—	—	100	590	46	—	—	—

Gas black (chloroprene rubber)[3]															
10	150	700	47	162	740	50	—	—	—	141	750	31	135	820	22
20	167	720	45	175	700	52	—	—	—	156	780	35	140	800	25
30	170	710	45	184	750	53	—	—	—	160	760	37	155	850	26
60	160	700	42	180	730	48	—	—	—	158	730	34	145	840	23
Thermal black (chloroprene rubber)															
10	103	800	39	110	700	43	—	—	—	100	750	35	89	700	29
20	109	820	40	118	770	42	—	—	—	95	740	31	90	730	31
30	115	820	38	124	760	44	—	—	—	90	700	40	86	750	30
60	105	820	43	120	790	40	—	—	—	99	720	37	83	760	28

[1] σ = tensile strength (in kg/sq cm); M—modulus at 300% elongation (in kg/sq cm); L—relative elongation in %.

[2] Formula (in parts by weight); SKS-30 (butadiene-styrene rubber with 30% styrene) 100 parts, sulfur 2, Altax 0.6, DPG 0.75, zinc oxide 5.0, stearic acid 2.0, Rubrax 5.0, carbon black 50.0.

[3] Formula (in parts by weight): Chloroprene rubber 100, zinc oxide 3.0, magnesium oxide 7.0, Rubrax 5.0, carbon black 50.0.

TABLE 4

INFLUENCE OF HEAT TREATMENT UPON THE ELEMENTAL COMPOSITION OF CARBON BLACKS

No.	Carbon black	Elemental composition in %		
		C	H	O
1	Gas black before heating	93.11	1.11	5.78
2	Gas black, treated at 20 to 1700° C for 4.5 h and at 1700° for 1.5 h	97.48	0.33	2.19

ties of vulcanizates based on SKS-30. There were even a 10 to 15% rise in the tensile strength.

It was interesting to investigate the influence of heat treatment upon the elemental composition of the carbon blacks and their specific surface.

The results of micro-elemental analysis of heat-tested chemical black carried out in the NIIShP (Tyre Research Institute), and the determination of the specific surface, carried out according to the method devised by Duzhanskii[15] are given in Tables 4 and 5.

From the data in Table 4 it may be seen that as a result of the high-temperature treatment of channel black the oxygen content fell to less than half, the hydrogen content to less than one-third. In hydrogen content the chemical black after heating approached the composition of the lamp and thermal blacks.

TABLE 5

INFLUENCE OF HEAT TREATMENT UPON THE SPECIFIC SURFACE OF CARBON BLACKS

No.	Conditions of heat treatment in ° C	Specific surface of carbon black (in sq m/g)		
		Gas	Lamp	Thermal
1	Without heating	85	16.5–24	23.3–21.6
2	Heating at 300°	87–90	26.3–29.0	—
3	Heating at 1200°	87–90	—	—
4	Heating at 1400°	59.3–52.4	23.3–21.6	—
5	Heating at 1700°	53.4–55.0	—	19.0–22.8

From the data in Table 5 it follows that as a result of heat treatment at 1400–1700° there took place a sharp reduction in the specific surface of the gas black and a practically insignificant alteration in the case of lamp and thermal black.

Thus the above data taken in conjunction show that heat treatment of gas black leads to a sharp deterioration in its reinforcing properties, the result both of the alteration in the microelemental composition and in the specific surface of the blacks.

INFLUENCE OF PRIOR HEATING OF MIXTURES OF CARBON BLACK WITH SULFUR AND ACCELERATORS UPON THE PHYSICAL PROPERTIES OF VULCANIZED RUBBER

It was necessary to investigate the influence of the products formed by interaction of the carbon black with sulfur and accelerators upon the physical properties of the vulcanizates[17].

With this aim the various mixtures of carbon black with sulfur and accelerators were subjected to prior heating at temperatures of 100 to 145° and were

TABLE 6

INFLUENCE OF PRIOR HEATING OF A MIXTURE OF LAMP BLACK, SULFUR AND ACCELERATOR UPON THE PHYSICAL PROPERTIES OF THE VULCANIZATES

Heated ingredients and conditions of heating	Curing conditions	Reference mixture			Experimental mixture		
		σ	L	1	σ	L	1
Carbon black + sulfur + MBT							
(SKB stock)							
	20 min at 143° C	56	565	23	71	472	15
1 h at 130° C	30 min at 143° C	62	525	21	74	382	9
	40 min at 143° C	64	457	15	74	336	8
3 h at 140° C	10 min at 155° C	62	317	—	78	487	—
	20 min at 155° C	67	235	4	90	360	6
	5 min at 170° C	63	370	10	74	500	12
	10 min at 170° C	59	237	4	95	467	16
Carbon black + sulfur + MBT							
(natural rubber stock)							
1 h at 130° C	15 min at 143° C	139	632	19	151	628	17
	20 min at 143° C	163	653	21	171	661	18
	30 min at 143° C	169	646	21	181	673	19
4 h at 130° C	15 min at 143° C	139	632	19	156	629	17
	30 min at 143° C	169	646	21	176	644	21
Carbon black + sulfur + MBT + TMTD							
(SKB stock)							
2 h at 130° C	10 min at 143° C	50	432	12	34	665	31
	25 min at 143° C	53	360	10	39	510	17
Carbon black + sulfur + MBT + DPG							
(SKB stock)							
	12 min at 145° C	52	382	11	76	450	15
	25 min at 145° C	64	176	4	82	275	7
2 h at 130° C	30 min at 145° C	65	235	4	86	290	4
Carbon black + sulfur + MBT + DPG							
(natural rubber stock)							
	8 min at 143° C	92	516	26	107	540	27
	12 min at 143° C	108	540	34	112	523	28
	15 min at 143° C	114	538	33	123	530	29
2 h at 130° C	20 min at 143° C	115	526	34	114	520	28
Carbon black + sulfur + MBTS							
(SKN-40)							
3 h at 100° C	15 min at 143° C	96	450	23	114	410	17
	30 min at 143° C	128	400	10	154	267	4
	60 min at 143° C	147	280	3	166	230	4
3 h at 150° C	30 min at 143° C	128	400	10	136	320	8
	60 min at 143° C	147	280	3	152	220	2
	90 min at 143° C	155	250	2	166	133	2

Note: σ—tensile strength (in kg/sq cm); L—relative elongation (in %); 1—permanent set (in %); SKB—sodium butadiene rubber, SKN-40—butadiene-acrylonitrile rubber with 36 to 40% of acrylonitrile.

then added to the rubber hydrocarbon. In parallel we prepared stocks by the ordinary procedure. The vulcanization of the experimental and reference stocks was carried out simultaneously in one mold. If as a result of the interaction of carbon black with sulfur and accelerators on the surface of the black active intermediate compounds (possibly also polysulfide compounds), reacting chemically with the molecules of the rubber and not decomposing before the beginning of vulcanization are indeed formed, it is not excluded that prior heating of the carbon black with sulfur and accelerators may lead to the production of stronger vulcanizates.

The results are shown in Table 6.

From the data presented we see that in the majority of cases prior heating of a mixture of carbon black with sulfur and accelerators gives vulcanizates with higher physical properties. In cases where a reduction in the properties is observed we evidently see decomposition of the intermediate compounds before the actual beginning of the process of vulcanization or else there takes place the formation of volatile products which do not reveal themselves in the vulcanizing system.

There is no doubt that the procedure of prior thermal activation of compounding ingredients offers prospects, since in future it will be possible to use molded briquettes, produced by prior thermal activation instead of powdered ingredients. This question calls for further study.

ISOTOPE EXCHANGE ON THE SURFACE OF CARBON BLACK PARTICLES

In our previous paper[12] we showed that in the process of vulcanization the free and polysulfidically bound sulfur enters into isotopic reaction with the atoms of sulfur in the structure of the accelerators. As a result of the isotopic exchange there takes place a separation of active fragments of sulfur which carry out acts of structurization of the rubber.

It was considered of interest to carry out isotopic exchange of the atoms of sulfur on the surface of the carbon black structure (this part of the work was carried out by O. Mamalsur).

With this aim radioactive sulfur was deposited upon the surface of the black from a benzene solution, after which the benzene was evaporated at room temperature. Then on the same particles MBT was deposited from an alcohol solution, and the alcohol was likewise evaporated at room temperature. Then the mixture of carbon black, radioactive sulfur and MBT was heated for 60 min at 130° C.

A reference test was arranged in a solution without carbon black under the same temperature conditions. As a result of measurements of the radioactivity of the extracted MBT it was found that the activity of the MBT in the experiment with the carbon black was 1260 impulses/min, while the activity of the MBT from the solution was 580 impulses/min, i.e., was considerably less.

It was shown by further investigation that the isotopic exchange of elementary sulfur and the mercapto sulfur of the MBT in the presence of carbon blacks (lamp, channel and furnace) leads to a marked increase in the intensity of isotopic exchange of the atoms of sulfur.

The most intensive isotopic exchange of the atoms of sulfur proceeds most intensively in the presence of lamp and furnace blacks.

Channel black, characterized by the acid pH value 3.52, falls short of furnace black which has the alkaline pH value 8.06. The results are shown in

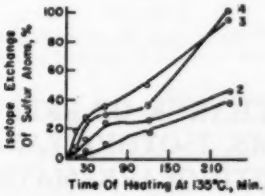


FIG. 6.—Isotopic exchange of sulfur atoms in the presence of carbon blacks (proportion of sulfur to MBT and carbon black 1:0.5:20): *1*—reference test without carbon black; *2*—gas black; *3*—furnace black; *4*—lamp black.

Figure 6. These data show that during vulcanization isotopic exchange in the vulcanizing stock procceds more intenisvely on the surface of the carbon black structure where the sulfur and accelerators are not only adsorbed but also chemically bound.

CONCLUSIONS

The experimental data collected on the interaction of active centers of carbon black with the rubber on the one hand and of the active centers of carbon black with the sulfur and accelerators, and also with the antioxidants, on the other hand, provide a sound basis for belief that the problem of reinforcement of rubber by active fillers in the process of vulcanization cannot be explained from the physical aspect alone.

The facts indicate the considerable importance of the chemical reactions between the active groups of carbon black and the compounding ingredients in the course of vulcanization.

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ISOTOPIC EXCHANGE OF FREE SULFUR WITH THIURAMS, ISOTHIOCYANATES AND DITHIOCARBAMATES *

L. S. Kuzina and E. N. Guryanova

Derivatives of dithiocarbamic acids ($R_2N—CS—SH$) are widely used as accelerators in rubber vulcanization, as insectofungicides, in pharmaceutical preparations, etc. Hence a study of the lability of sulfur atoms in these compounds assumes significant interest, not only in clarification of general questions of structure and reactivity, but also in finding a rational approach to their use in chemical practice.

The literature cites data for isotopic sulfur-exchange in tetramethylthiuram disulfide[1–3], methyl dithiocarbamate and sodium diethyldithiocarbamate[4], as well as brief reports of ours[5] on sulfur exchange in several thiurams, esters and salts of dithiocarbamic acid.

The present work represents a continuation and development of previous research[3, 5–7], in attempting to ascertain the influence of certain structural factors upon the exchangeability of sulfur atoms in the thiurams and dithiocarbamate esters. First of all in importance is the clarification of the following questions: (1) of what significance is an increase in the number of sulfur atoms in the thiurams (mono-, di-, tri- and tetrasulfides) when considering exchange with elemental sulfur; (2) how does a change in the radicals on the amino group influence the lability of the sulfur atoms which are not directly attached to the group $R_2N—CS—S$; (3) what is the relationship between sulfur exchangeability in the dithiocarbamate derivatives ($R_2N—CS—SH$) as compared with that of the analogous xanthogenates ($R—O—CS—SH$). Our studies of the isotopic exchange of sulfur between the thio-compounds on the one hand, and elemental, radioactive sulfur on the other, has taken two approaches: to establish the optimal reaction conditions for exchange, with determination of the number of exchangeable sulfur atoms in the materials studied, and also, in certain systems, to measure the kinetics of the exchange at various temperatures.

EXPERIMENTAL

Syntheses, methods of purification and constants of the materials utilized in this work were published previously[6] in a report dealing with the polar properties of these compounds.

The isotopic exchange experiments were carried out in solution, although in certain cases without use of a solvent but rather in ampules. Methods for separating components after the exchange were varied for different systems; in some including tetramethylthiuram monosulfide-sulfur, tetramethylthiuram trisulfide-sulfur, tetrabutylthiuram disulfide-sulfur, Diproxid (di-isopropylxanthodisulfide)-sulfur the difference in solubility of the organic compound and of sulfur in acetone or methanol was utilized as a means of separation, while in other systems including Tetron (Compound No. 4, Table III)-sulfur and tetra-

* Translated by J. R. Robinson from *Zhur. Fiz. Khim. SSSR* 33 (9), 2030–2035 (1959).

TABLE I

EQUILIBRIUM DISTRIBUTION OF RADIOACTIVITY IN THE SYSTEMS: THIURAM: SULFUR, 1 MOLE: 4 ATOMIC WTS

Thiuram disulfide	Original sulfur	After exchange		Calc'd. for exchange of	
		Sulfur	Thiuram	4S	2S
Tetramethyl-	2624	1308	1312	1312	875
Tetra-*n*-butyl-	1168	572	595	584	389
Tetra-*iso*-butyl-	1232	628	608	616	411
Symm. diphenyldimethyl-	640	326	320	320	213
Tetraphenyl-	672	332	348	336	224
Diproxid	1184	603	587	592	395

phenylthiuram disulfide-sulfur we utilized the different temperature coefficients of solubility of organic material and of sulfur in toluene, benzene or decalin. In another pair of systems comprising ethyl dithiocarbamates-sulfur and isothiocyanates-sulfur the components were separated by vacuum fractionation. As a rule, the constants of the materials isolated after the exchange conformed to the constants of the starting materials.

The number of exchangeable atoms of sulfur in the compounds was determined by comparison of the relative activities of the components of the mixture at equilibrium. Equilibrium in the different systems was reached under the conditions outlined in Table III, and the results of measuring the radioactivity (as benzidine sulfate precipitate) at equilibrium between the thiurams and sulfur are given in Table I along with the activities calculated for the exchange of two or four atoms of sulfur in the thiuram.

The distribution of radioactive sulfur at equilibrium in the dithiocarbamate-sulfur mixtures is indicated in Table II beside the calculated values expected in the exchange of one or both sulfur atoms.

A resumé of experimental results for the exchange studies in all the compounds is given in Table III. In the first column are the formulas of the compounds labeled by exchange with radio-sulfur, the solvent used, and the concentration of the material C_B in g mole/liter and sulfur C_s in g atom/liter. The other columns indicate the temperature, the time, the degree of exchange (%), the velocity constant (in sec.$^{-1}$) for the exchange and the activation energy (E) in kcal/g mole.

The exchange reactions involving sulfur and tetramethylthiuram monosulfide (1, Table III) and trisulfide (3, Table III) are accompanied by side reactions; the addition of sulfur to form a disulfide in the first case, and the formation of a thiuram with a different sulfur content in the second. Such conversions render difficult any measurement of kinetics having a quantitative character.

In the Tetron molecule (4, Table III) four of the sulfur atoms are bonded to carbon, two to sulfur, and it is of interest to clarify which one initiates the

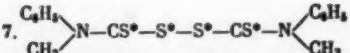
TABLE II

EQUILIBRIUM DISTRIBUTION OF RADIOACTIVITY IN THE SYSTEMS: DITHIOCARBAMATE: SULFUR, 1 MOLE: 1 ATOMIC WT

$R_2N—CS—SC_2H_5$	Original	After exchange	Calc'd for exchange of	
			1S	2S
Dimethyl-	454	225	227	151
Diethyl-	822	412	411	274
Di-*n*-Butyl-	1068	532	534	356

TABLE III

EXCHANGE WITH ELEMENTAL RADIOACTIVE SULFUR

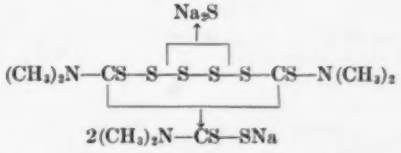
Compound	t° C	Time Hours	Exchange %	k×10⁴	E
1. $(CH_3)_2N—CS^*—S^*—CS^*—N(CH_3)_2$	80	3	0	—	—
бензол, $c_B = c_S = 0{,}1$	130	5	85	—	—
2. $(CH_3)_2N—CS^*—S^*—S^*—CS^*—N(CH_3)_2$ *	110	—	—	0,24	
нафталин, $c_B = 0{,}1$, $c_S = 0{,}2$	120	—	—	0,42	
	130	—	—	0,87	(21,4)
	136,5	—	—	1,95	
	150	—	—	7,10	
3. $(CH_3)_2N—CS^*—S^*—S^*—S^*—CS^*—N(CH_3)_2$	110	10	85	—	—
толуол $c_B = c_S = 0{,}1$					
4. $(CH_3)_2N—CS^*—S^*—S^*—S^*—S^*—CS^*—N(CH_3)_2$	80	3	0	—	
толуол, $c_B = c_S = 0{,}1$	90	6	50	—	
	100	6,5	75	—	—
	110	6	90	—	
	110	12	100	—	
5. н-$(C_4H_9)_2N—CS^*—S^*—S^*—CS^*—N(C_4H_9)$-н	130	—	—	1,3	—
бензол, $c_B = 0{,}1$, $c_S = 0{,}4$					
6. *изо*-$(C_4H_9)_2N—CS^*—S^*—S^*—CS^*—N(C_4H_9)$-*изо*	110,5	—	—	0,5	
бензол, $c_B = 0{,}1$, $c_S = 0{,}4$	120,5	—	—	1,0	
	133,5	—	—	2,5	
	136	—	—	2,8	23,8
	144	—	—	6,0	
	148,5	—	—	7,8	
7. 	131	—	—	0,6	
	138	—	—	1,0	
бензол, $c_B = 0{,}1$, $c_S = 0{,}4$	141	—	—	1,5	26,7
	150	—	—	2,6	
8. $(C_6H_5)_2N—CS^*—S^*—S^*—CS^*—N(C_6H_5)_2$	132,5	—	—	0,6	
толуол, $c_B = 0{,}03$, $c_S = 0{,}015$	146	—	—	1,8	27,8
	168,5	—	—	10,0	
9. $C_3H_7—O—CS^*—S^*—S^*—CS^*—O—C_3H_7$	80	10	0	—	
бензол, $c_B = c_S = 0{,}1$	115	5	100	—	
10. $(CH_3)_2N—CS^*—SC_2H_5$	147	—	—	0,3	
декалин, $c_B = c_S = 0{,}31$	153	—	—	0,6	41,9
	160	—	—	1,8	
	172,5	—	—	6,1	
11. $(C_2H_5)_2N—CS^*—SC_2H_5$	140	—	—	0,2	
декалин, $c_B = c_S = 0{,}31$	146	—	—	0,4	
	160	—	—	1,2	30,4
	170	—	—	2,8	
	174,5	—	—	4,5	
12. $(C_4H_9)N—CS^*—SC_2H_5$	139	—	—	0,9	
декалин, $c_B = c_S = 0{,}31$	149	—	—	2,0	25,6
	160	—	—	4,0	
	170	—	—	9,0	
13. $C_6H_5NH—CS^*—SC_2H_5$ **	150	12	50	—	
декалин, $c_B = c_S = 0{,}31$					
14. $C_2H_5N=C=S^*$ **	150	6	0	—	
декалин, $c_B = c_S = 0{,}47$	165	3	15	—	
	180	6	100	—	
15. $C_6H_5N=C=S^*$ **	150	6	0	—	
	165	3	15	—	
	180	6	100	—	

* Results published earlier[3].
** Exchange accompanied by some decomposition.

TABLE IV

Material	Radioactivity of samples, counts/minute					
	80° 3 Hr.	90° 6 Hr.	100° 6¼ Hr.	110° 6 Hr.	110° 12 Hr.	Calc'd equilib'm
Orig. sulfur	1280	1168	1248	1104	1050	1050
Sulfur after exch.	1280	253	272	176	153	150
Tetron after exch.	0	115	128	160	152	150
Copper dimethyl-dithiocarbamate	—	83	88	149	147	150
Copper sulfide	—	182	208	—	150	150

sulfur exchange, and to what extent the velocity of the exchange differs in these non-equivalent sulfur atoms. In determining the activity of the various sulfur atoms we employed a degradation reaction using sodium amalgam in alcohol. The two central sulfur atoms thus appear as sodium sulfide and the outer ones, attached to carbon, show up as sodium dimethyldithiocarbamate:



The mixed sodium salts were precipitated by a buffered solution of copper sulfate, dried and then the copper dimethyldithiocarbamate was extracted with toluene, while the copper sulfide remained in the residue. After additional purification the components were oxidized by Carius' method and the sulfur precipitated by a solution of benzidine hydrochloride. The activities of the samples obtained from the various components, in the ratio of one mole of Tetron to one atom of sulfur, are given in Table IV, along with reaction conditions and the calculated activity expected at equilibrium for all the sulfur atoms.

DISCUSSION OF RESULTS

The data of Table III shows that the exchangeability of sulfur with the dithiocarbamate derivatives depends to a significant extent upon the composition and structure of the material. In the thiurams ($R_2N—CS—S—S—CS—NR_2$) the exchange with elemental sulfur proceeds with measurable velocity at 110°–120°, whereas the esters ($R_2N—CS—SR$) do not exchange at these temperatures. These begin only at 140–150°, and the isothiocyanates ($RN{=}C{=}S$), having a group of atoms similar to the dithiocarbamates, undergo exchange only at 160–170° with partial decomposition. The influence of various factors on the exchange process were considered in greater detail in each group of materials. First of all was examined the quantitative exchangeability of the sulfur atoms. Regarding the thiurams, two observations are already reported; that they exchange two[2], and that they exchange four[3] sulfur atoms. This point is discussed in A. I. Brodskiĭ's monograph[5].

The data of Table I are in complete accordance with our earlier work[2] and fully confirm our contention that four atoms of sulfur are exchanged in all the thiurams, independant of the nature of the radicals. We are of the opinion that this matter of the equivalent exchangeability of all four sulfur atoms is adequately clear and requires no further discussion. The exchange of four atoms

of sulfur occurs, too, in the molecule of di-isopropylxanthodisulfide (Diproxide, compound 6, Table I). In Tetron (4, Table III), six atoms of sulfur are exchanged but, in contrast to the thiurams, not all of these sulfur atoms are equivalent with regard to their exchangeability. As seen in Table IV the two central atoms, converted on reduction to sodium sulfide, are exchanged to a significantly lesser degree than the remaining four sulfur atoms which are bonded to carbon atoms. It should be noted that, in contrast to the simple polysulfides (R—S—S—S—S—R) where there is an abrupt difference between the exchangeability of sulfur atoms with a C—S bond and those in S—S bond, in Tetron this difference is not large and there is practically no way of differentiating the two kinds of sulfur atoms. At 100° there was a significantly rapid exchange of the central sulfur atoms, but a very slow exchange of the outer atoms. On reaching equilibrium the activities of these two kinds of sulfur had become equal. In contrast to the thiurams the dithiocarbamate esters, as shown by the data of Table II and in agreement with earlier findings[4, 5], exchange only one sulfur, obviously the C=S sulfur, the alkyl-bonded sulfur being unaffected.

As the number of atoms in the polysulfide chain increases, the exchange rate increases, as measured in compounds 1, 2, 3 and 4 of Table III where the degree of ease of exchange increases:

$$\text{mono} \leqslant \text{di} < \text{tri} < \text{tetrasulfide}$$

In comparing the sulfur exchange which occurs in the thiuramdisulfides having different alkyl radicals, R, (compounds 2, 5, 6 7 and 8 of Table III) it is found that the substitution of one aliphatic radical for another has little effect, but replacement of an aliphatic by an aromatic radical, especially a phenyl radical, depresses the exchange rate. In thiurams with all aliphatic radicals the exchange proceeds at a measurable velocity at 110° whereas with dimethyldiphenylthiuram disulfide the exchange approaches the same velocity only at 130°, and tetraphenylthiuram disulfide requires an even higher temperature. This is tied in with the activation energy; introduction of a phenyl radical into the amino group of the thiuram molecule causes a strengthening of the C—S bond. This point assumes great interest in the investigation of the effect of different substituents on the exchangeability of the sulfur of thiurams possessing aromatic radicals. In contrast to the thiurams, in the dithiocarbamates there are observed few such regularities in the influence of different substituents. If first one aliphatic radical is substituted for another practically no effect is noted upon the sulfur exchangeability, but if the structure is altered markedly, a substantial influence upon the rate of exchange is found. (Compounds 10, 11, 12 and 13, Table III). In the group of ethyl dithiocarbamates, on passing from compounds with dimethyl radicals (R_2, in R_2N—CS—S—Et) to those having diethyl and dibutyl groups, the exchange of sulfur should be facilitated, the energy of activation for the exchange being 41.9, 30.4 and 25.6 kcal/mole, respectively. The difference between the regularity of the influence of radicals on sulfur lability in the thiurams and that in the dithiocarbamate esters probably indicates that the mechanism of sulfur-exchange is different in these two types of compound. In the thiurams, as we considered earlier[3] agreeing with other work[2], the exchange proceeds through a dissociation mechanism with rupture of the C—S bond while in the esters, the sulfur exchanges in the C=S group, obviously via an association mechanism similar to that put forward by Miklukhin et al.[4].

The conditions for sulfur exchange in di-isopropylxanthodisulfide (compound 9, Table III) are approximately the same as those for the corresponding thiuram, consequently the replacement of an amino group by alkoxy does not cause any abrupt alteration in the exchangeability of the —C(S)S structure. However, experimental evidence collected is too small to allow further conclusions on this subject.

Many dithiocarbamate derivatives are utilized in the vulcanization of rubber; in this connection it is of interest to compare their ability to exchange sulfur atoms with their activity in the vulcanization process. Since vulcanization is a complex, multicomponent reaction depending upon a series of factors we can hardly expect to find a straight-forward connection between vulcanization accelerator activity and the ability to exchange atoms with elementary sulfur. However, by comparing data collected upon various groups of compounds we may note some parallelisms in these two processes because they may be based upon one elementary reaction. With this in mind, examination of the data of Table III leads to the conclusions that thiurams which are rich in sulfur ought to be more effective as accelerators and vulcanizers than those having less sulfur in the molecule; however, this will be modified by the solubility of the compounds in rubber. Thiuram disulfides with aromatic radicals ought to be less active than thiurams with aliphatic radicals. Dithiocarbamate esters should not possess vulcanization accelerator properties.

SUMMARY

1. Studies were made concerning the exchangeability, with elementary radioactive sulfur, of sulfur atoms in 15 compounds including thiurams, dithiocarbamate and isothiocyanates. The number of exchangeable sulfur atoms in each material was established, as well as the optimal conditions for exchange, and for seven of the compounds the activation energy for the process was determined. The exchange rate of thiurams, with elementary sulfur, increases with the number of sulfur atoms in the polysulfide chain. In tetramethylthiuram tetrasulfide the two middle sulfur atoms are more readily exchanged, while the outer four sulfurs, bonded to carbon, are exchanged less rapidly but not sufficiently so to allow carrying out a separate exchange.

2. The velocity of exchange is significantly reduced in the thiuram disulfides when aliphatic radicals are replaced by phenyl radicals. A difference in the influence of amino-group radical variations was noted between the thiurams and the dithiocarbamates.

The results of the isotopic exchange of sulfur in these materials have been considered from the viewpoint of their effectiveness as accelerators in the vulcanization of rubber.

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VULCANIZATION OF ELASTOMERS. 30. KINETICS OF THE DECREASE OF SULFUR CONCENTRATION DURING VULCANIZATION *

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INTRODUCTION

In discussions of the character of the crosslinking in natural rubber and in synthetic poly-1,5-dienes[1], there is always interest in the question about the regularities which are shown by the decrease in sulfur concentration with reaction time for various temperatures and concentrations of reactants, both in accelerated and unaccelerated vulcanizations; for the results at hand touching on this matter are incomplete and the prevailing ideas on the subject are not sufficiently well established. In years gone by, we have consequently carried on systematic research, attempting to bring clarity into this matter and also seeking to show a connection of the already found relations with the crosslinking reaction in so far as the latter can be measured by the change in the equilibrium swelling with vulcanization time. Several kinetic characteristics have shown up here with respect to the decrease of sulfur concentration, which are peculiar to a series of vulcanization reactions. We have described them variously in several practical examples and have sought to clarify them as well as to think them through from a theoretical viewpoint[2].

The discussions centered about the conclusion reached through the kinetic results for the decrease of sulfur concentration in several accelerated vulcanizations that the reaction between rubber and sulfur takes place through an intermediate compound. The characteristic dependence of the initial rate of sulfur-disappearance upon the initial concentration of sulfur particularly concerned us and suggested that, for its explanation, we draw upon the ideas developed by Michaelis and Menten[3] as well as by Briggs and Haldane[4] about the course of catalysis by intermediate compounds. In this regard, we more or less limited ourselves to the indication of a formal agreement between our experimental results and the theory.

In the meantime, extensive experimental material has accumulated in this field so that it will be appropriate to present it both comprehensively and critically with especial consideration of the theoretical treatment and interpretation. In doing this, we will first confine ourselves to the kinetics of the disappearance of sulfur during vulcanization reactions.

KINETICS OF THE DECREASE OF SULFUR CONCENTRATION IN ITS REACTION WITH RUBBER

If at first we ask about the nature of the kinetics of sulfur disappearance in a vulcanization without accelerator or under any other circumstances, it is natural to assume that a bimolecular reaction takes place. However, since

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rubber is usually present in very great excess during the vulcanization reaction, we should find experimentally that the reduction in sulfur concentration follows a time law of the 1st order, so that we have a pseudo monomolecular reaction. Order of reaction and molecularity would then not be identical. But if the spontaneous, thermal breaking of the S_8 ring were the characteristic, rate-determining step of the reaction, then the sulfur concentration would decrease according to a 1st order law; reaction order and molecularity would then be identical.

So long as nothing more takes place than has been suggested above, we can depend upon it that the sulfur concentration will fall according to a 1st order law. For this it must merely be assumed that the sulfur is completely dissolved in the rubber, otherwise it would react entirely or in part according to a time law of zero order.

We will find somewhat different relations holding if the reaction products affect the rate of sulfur decrease, by either increasing or decreasing it. Other orders of reaction will then be found, and there can then exist no agreement between the time law and the concentration-dependence of the rate. Particularly when catalysis by the reaction products takes place must exponents of the time law be reckoned with which fall between 0 and 1. We ask how and to what extent we can secure experimental clarification as to what actually occurs and recall several fundamental facts of kinetics to help in our understanding. Because of the usual great excess of rubber present in a vulcanization we have experimental conditions such that we get information about the exponent in the time law with respect to the one reactant, sulfur, just by measuring the change, with time, of the sulfur concentration. Whether the overall order of reaction is determined at the same time cannot be decided for the time being by taking into account the aforementioned considerations.

The decrease in sulfur will now follow the generally valid equation for a reaction of the nth order:

$$dx/dt = k(a - x)^n \tag{1}$$

In Equation (1) which defines the dependence of the rate upon concentration, a is the initial concentration of the reactant, x is the reacted portion of it, t is the reaction time and n is a whole number or fraction, representing the order of the reaction. We can evaluate n in proper manner[5], and can test its correctness by plotting the research data, introducing n in accordance with the integral of Equation (1), the time law.

We have

$$1/(a - x)^n dx = kt + c$$

With the initial conditions $t = 0$ and $x = 0$, we have when $n \neq 1$

$$1/(1 - n)(a - x)^{1-n} = - kt + 1/(1 - n)a^{1-n} \tag{2}$$

and when $n = 1$ we have

$$\log (a - x) = - kt + \log a \tag{3}$$

also, for $n = 0$, we have

$$dx/dt = \text{const.} \tag{4}$$

When n is accurately determined we can plot $1/(1-n)(a-x)^{1-n}$ or $\log (a-x)$ against reaction time t and obtain a linearly decreasing function provided that $n \gtrless 1$. The rate constant $k^{(n)}$ can be determined from the slope of the line. However, if $n > 1$ we would obtain an ascending straight line when the experimental data are plotted against reaction time according to Equation (2).

This shows that the rate constant is independent of the initial concentration of the reactant under consideration, in which case, graphic presentation of the data according to Equation (2) or Equation (3) gives a group of parallel straight lines for various values of a. A straight line is also obtained by plotting the initial rate $(dx/dt)_0$ against the nth power of the initial concentration, and there exists agreement between the time law and the concentration dependence of the rate.

Experience shows, however, that this agreement is not often encountered, that is—to use an expression of Laidler[6]—there exists a discrepancy in the order with respect to time and concentration. The reason for this must be looked upon among other things, as the effect of the reaction products on the rate. Two different cases for this may be distinguished. When an increase in the rate takes place (catalysis by the reaction products), the time law has a smaller exponent than that of the concentration dependence of the rate. However, if the rate is diminished (inhibition by the reaction products), then the time law has a larger exponent than the concentration dependence of the rate. In both cases, the rate constant, as determined by the time law, is dependent upon the initial concentration, and increases, for example, in the presence of catalysis.

Now the course of every chemical reaction is best defined at the beginning, hence the dependence of the rate on concentration is of increasing importance; in particular, the character of the reaction should be most clearly expressed in the relations between initial concentration and initial rate. Actually, the "true" reaction order is found only in this way, so that it is important, in complex cases, to differentiate sharply between the "true" order of the reaction (exponent n of the dependence of initial rate on concentration) and the exponent of the time law.

In the case of pure sulfur vulcanization (in the absence of all other additives) it appears that the sulfur, as long as it is completely dissolved in the rubber, disappears in accord with a time law having $n = 0.6$ as exponent[7]. This holds for all temperatures and is independent of initial concentration. At the same time, however, the rate constant $k^{(0.6)}$ is an increasing function of the initial concentration of sulfur, thus showing a lack of agreement between the time law and the dependence of the initial rate on concentration.

So we have next:

$$d(S_8)/dt = k'[(S_8)_0 - (S_8)_e]^{0.6} \tag{5}$$

$$1/(1-0.6)[(S_8)_0 - (S_8)_e]^{1-0.6} = -k't + 1/(1-0.6)(S_8)_0^{1-0.6} \tag{6}$$

In Equations (5) and (6), $(S_8)_0$ is the initial concentration of sulfur, $(S_8)_e$ the reacted portion of the sulfur and k' is the rate constant which is dependent upon the initial concentration of sulfur. By putting the determined values of k' and the appropriate values of initial concentration into Equation (5), the initial rate of sulfur-disappearance is given by Equation (7).

$$[d(S_8)/dt]_0 = k'(S_8)_0^{0.6}. \tag{7}$$

If these are plotted against initial concentrations of sulfur, a straight line through the origin results, which indicates that Equation (8) applies; in other words, sulfur disappearance is of the 1st order,

$$[d(S_8)/dt]_0 = k(S_8)_0 \tag{8}$$

so the true order is $n = 1$. Therefore—as has been previously stated—a pseudo monomolecular reaction between rubber and sulfur or else a monomolecular splitting of the S_8 ring takes place. Which of these two possibilities is true, cannot be decided from the kinetic results, because rubber is present in great excess. Only studies of the reactions of model compounds with sulfur under conditions of comparable concentrations of the reactants can throw further light on this. Such studies have been made by Farmer and coworkers, and in more recent times by Bateman, Moore, Glazebrook, Saville and others[8]. But the determination of the composition of the resulting products has been emphasized in these studies, while kinetic investigations have been published only recently.

Now since—as experimentation broadly teaches—the time law shows a smaller exponent ($n = 0.6$) than that for the dependence of the rate on concentration ($n = 1$), it is to be inferred that catalysis of sulfur disappearance by the reaction products must take place, which is to say that the decrease of sulfur concentration is an autocatalytic process. This conclusion, in our opinion, is compelling; for the lack of agreement between the time law and the concentration dependence of the rate of sulfur disappearance can scarcely be explained except by the direct effect of the reaction products on the rate. If a question is raised about the identity of the reaction products which bring about the catalysis, the sulfur bound as polysulfide at the crosslinking sites may be involved.

KINETICS OF THE DECREASE OF CONCENTRATION OF SULFUR IN ACCELERATED VULCANIZATIONS

When accelerators are used in a vulcanization, somewhat different kinetic relations are met with. It will be appropriate to assemble their prominent characteristics and compare them with unaccelerated vulcanizations in order to then attempt an explanation.

It is evident that the decrease of sulfur even in an accelerated vulcanization can be expressed by a time law with a fractional exponent. It is found that exponent values lie between 0.6 and 0.8, and this is independent of temperature as well as of initial concentrations both of sulfur and accelerator. This is also true whether natural or synthetic rubber is used[9].

In accelerated vulcanizations, the dependence on concentration of the initial rate of sulfur decrease deserves special attention. Concerning this, it is evident that initial rate and rate constants for sulfur decrease are dependent upon the molar proportions of accelerator and sulfur in the rubber. Thus we have the following state of affairs[9].

1) With constant initial concentration of sulfur and increasing accelerator content, the initial rate of sulfur disappearance rises sharply at first, to become practically constant when the accelerator is present in considerable excess (see the schematic diagram in Figure 1). Then the rate constant for sulfur disappearance follows the same course as the accelerator content, since $(S_8)_0 =$ const.

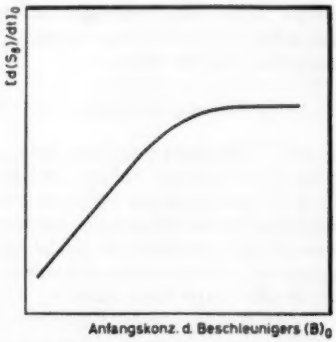

FIG. 1.—Schematic representation of the dependence of the initial rate of sulfur decrease upon the accelerator content (sulfur concentration constant). Ordinate: as given on figure. Abscissa: Initial concentration of accelerator $(B)_0$.

2) With constant initial accelerator content and increasing initial sulfur concentration, the initial rate of sulfur decrease rises sharply at first, to become practically constant when sulfur is in considerable excess (see the schematic diagram in Figure 2). It is seen that the rate constant for sulfur decrease becomes smaller with increasing initial concentration of sulfur; and from this it follows that the initial rate shows a smaller rise with the initial concentration of sulfur than the time law requires.

The collection of data in Table I gives a general view of the vulcanization reactions which have been studied closely by us up to this time. It should be emphasized, that the natural rubber (pale crepe) as well as the Perbunan (first Column of the Table), used in the experiments, had been carefully purified by exhaustive extraction with acetone or alcohol. The accelerators such as CMBTS (N-cyclohexyl-2-benzothiazyl sulfenamide) as well as MBTS (2-benzothiazyl disulfide) were purified thoroughly by recrystallization or fractional distillation. Particular attention is called to the information in Columns

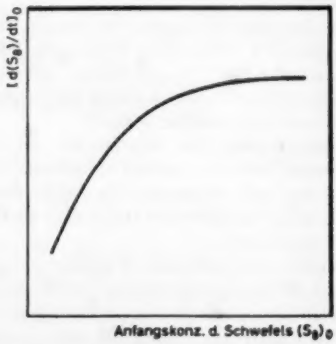

FIG. 2.—Schematic representation of the dependence of the initial rate of sulfur decrease upon the sulfur concentration (accelerator content constant). Ordinate: as given. Abscissa: Initial concentration of sulfur $(S_8)_0$.

TABLE I

TIME LAW, CONCENTRATION DEPENDENCE OF THE RATE, AND ACTIVATION ENERGY FOR SULFUR DECREASE IN ACCELERATED VULCANIZATION OF NATURAL RUBBER AND PERBUNAN [1]

System	Vulcanization temp., ° C	$(S_8)_0$ m moles per 100 g compound	Accelerator m moles/100 g compound	Exponent n of the time law	Concentration dependence of initial rate, reaction order	Apparent activation energy, Q_A kcal/mole
Pale crepe, sulfur	140–160 5 Series	12.5		0.6		~35
Pale crepe, sulfur	150	3.125–75 15 series		0.6 for 3.125 to 24 m mole S_8; at higher S_8 concentrations for initial range, zero order with autocatalysis	1st order in the range of full solubility of sulfur	
Pale crepe, sulfur, zinc oxide	140–160 5 series	12.5		0.6		
Pale crepe, sulfur, DPG	100–140 8 series	10	10	0.75		29.8
Pale crepe, sulfur, DPG	115	10	2.4 to 28.5 8 series	0.7	Course according to intermediate compound catalysis	
Pale crepe, sulfur, DPG	140	10	2.0 to 40.0 9 series	0.7	Course according to intermediate compound catalysis	
Perbunan N2818, sulfur, DPG	100–130 7 series	10	10	0.8		~28

[1] Previously unpublished series using natural rubber with MBTS ,CMBTS or cyclohexylamine and MBT or DPG plus zinc oxide, were from the work of K. H. Muller, G. Kerrutt, and H. Schafer, respectively.

TABLE I—(*Continued*)

System	Vulcanization temp., ° C	$(S_8)_0$ m moles per 100 g compound	Accelerator m moles/100 g compound	Exponent n of the time law	Concentration dependence of initial rate, reaction order	Apparent activation energy, Q_A kcal/mole
Perbunan N2818, sulfur, DPG	115	10	2.0–150.0 14 series	0.8	Course according to intermediate compound catalysis	
Perbunan N2818, sulfur DPG	130	10–35 6 series	10	0.8	Course according to catalysis by intermediate compound	
Pale crepe, sulfur, zinc oxide (150 m moles/100 g), DPG	110–140.6 7 series	10	10	0.8		27
Pale crepe, sulfur, zinc oxide (150 m moles/100 g), DPG	115	10	2.5 to 50 8 series	0.8	Course according to catalysis by intermediate compound	
Pale crepe, sulfur, zinc oxide (150 m moles/100 g), DPG	130	2.5 to 60	50	0.8	No general law of exponents	
Perbunan N2818, sulfur, CMBTS	100–130 7 series	10	10	0.8		28.2
Perbunan N2818, sulfur, CMBTS	115	5–30 8 series	10	0.8	In accordance with catalysis by intermediate compound	

TABLE I—(*Continued*)

System	Vulcanization temp., °C	$(S_8)_0$ m moles per 100 g compound	Accelerator m moles/100 g compound	Exponent n of the time law	Concentration dependence of initial rate, reaction order	Apparent activation energy, Q_A kcal/mole
Perbunan N2818, sulfur, CMBTS	115	10	1.25 to 30 8 series	0.8	In accordance with catalysis by intermediate compound	
Perbunan N2818, sulfur, cyclohexylamine-MBT	100–130 4 series	10	10	0.8		28.2
Pale crepe, sulfur, CMBTS	110 to 140 7 series	10	10	0.7		29.7
Pale crepe, sulfur and amine[2]	140	10	10	Varying from 0.5 to 0.7		
Perbunan N2818, sulfur, and amine[3]	130	10	10	0.8		
Pale crepe, sulfur, aniline	140	10	1.0–40.0 8 series	0.7	According to catalysis by intermediate compound	
Pale crepe, sulfur, MBTS	115 to 140 6 series	10	10	0.8		30.5
Pale crepe, sulfur, MBTS	120	10	2.5 to 30 7 series 2.5 to 10 15.0 to 30.0	 0.8 1.0	Special relations, at present not clear	~28

[2] Dimethylaniline, diethylaniline, methylaniline, ethylaniline, 1-naphthylamine, *o*-toluidine, *m*-toluidine, *p*-toluidine, aniline, benzylamine, or DPG.
[3] Benzylamine, dibutylamine, diisobutylamine, diethanolamine, or ethanolamine.

TABLE I (*Continued*)

System	Vulcanization temp., ° C	$(S_8)_0$ m moles per 100 g compound	Accelerator m moles/100 g compound		Exponent n of the time law	Concentration dependence of initial rate, reaction order	Apparent activation energy, Q_A kcal/mole
Pale crepe, sulfur, MBTS	120	4.5 to 50 8 series				Special relations, at present not clear	
		5.0 to 7.5	—	—	1.0		~28
		10.0 to 50	—	—	0.8		
Pale crepe, sulfur, MBT cyclohexylamine	120–135 5 series	10	10 m moles MBT/100 g, 10 m moles cyclohexylamine/100 g		0.45		29.0

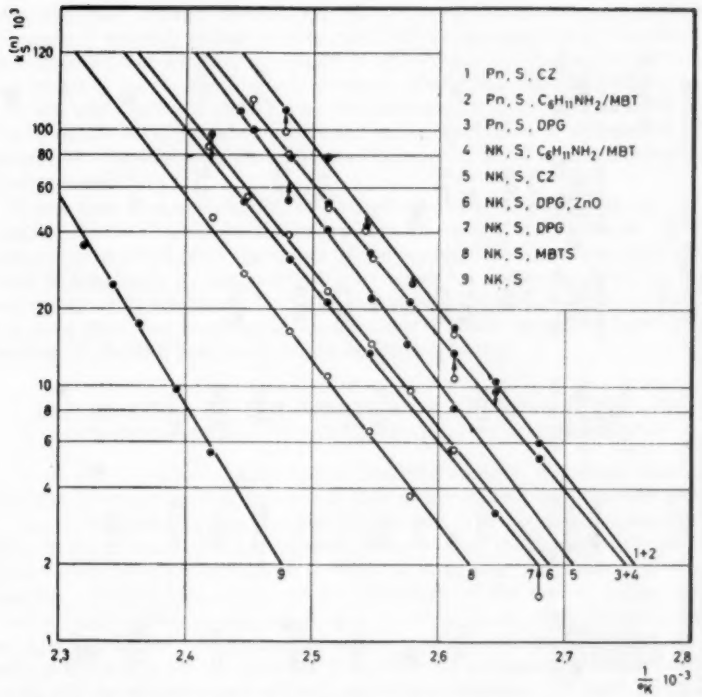

FIG. 3.—Temperature functions of the rate constants for sulfur decrease in several accelerated vulcanizations (10 m moles S_8 and 10 m moles accelerator). Pn = Perbunan; NK = natural rubber. CZ = N-cyclohexyl-2-benzothiazyl sulfenamide or CMBTS. MBT = Mercaptobenzothiazole. MBTS = 2,2'-dibenzothiazyl disulfide. DPG = Diphenylguanidine. S = Sulfur. Ordinate and Abscissa: as given.

5 and 6 concerning the exponents of the time law and the dependence on concentration of the initial rate.

Table I does not include results obtained by Lorenz and Echte for vulcanization of natural rubber in the presence of MBT (mercaptobenzothiazole) plus zinc oxide or of MBT, zinc oxide and zinc stearate[10]. Likewise, the results of vulcanization accelerated by zinc dithiocarbamate[11] are not given here. Data found in these cases are more complicated even if not fundamentally different.

Since, as has already been stated, the rate of sulfur decrease depends upon the molar ratio in which sulfur and accelerator are present, it is difficult to make any definite statement about the increase which is brought about by a given accelerator. We can get an approximate idea however, if we consider the dependence on temperature of the rate constant for sulfur decrease under conditions of identical molar concentrations of sulfur and accelerator. In Figure 3 we have plotted the rate constants (log scale) against the reciprocal of the absolute temperatures of vulcanization, for cases in which 10 m moles S_8 and 10 m moles of accelerator were used for each 100 g of rubber compound. The greatest variation found in the rate constants amounts to about 1.5 powers of ten, and is, accordingly, considerable. It will be noticed that MBTS brings

Table II

Rate Constants of Sulfur Decrease $k_S(n)\cdot 10^3$ for Vulcanization of Natural Rubber or Perbunan in the Presence of Accelerators (10 m moles S_8 and 10 m moles Accelerators in 100 g Compound)—K. Scheele and coworkers

Temperature		Pale crepe, sulfur* $k_S^{(0.6)}\cdot 10^3$	Pale crepe, sulfur, MBTS $k_S^{(0.8)}\cdot 10^3$	Pale crepe, sulfur, DPG $k_S^{(0.75)}\cdot 10^3$	Pale crepe, sulfur, DPG, 150 m moles ZnO/100 g $k_S^{(0.5)}\cdot 10^3$	Pale crepe, sulfur, CMBTS $k_S^{(0.7)}\cdot 10^3$	Pale crepe, sulfur, MBT, cyclohexyl-amine $k_S^{(0.45)}\cdot 10^3$	Perbunan, sulfur, DPG $k_S^{(0.8)}\cdot 10^3$	Perbunan, sulfur, MBTS $k_S^{(0.8)}\cdot 10^3$	Perbunan, sulfur, cyclo-hexyl-amine-MBT $k_S^{(0.8)}\cdot 10^3$
$\frac{1}{°K}$	°C									
0.00268	100			1.53				5.2	6.0	10.2
0.002645	105			3.19				8.6	10.5	
0.002613	109.8					8.28	11.82			
0.002612	110			5.63	5.60			13.77	17.0	16.0
0.002578	115		3.74		9.62			21.5	25.0	
0.002575	115.16					14.5				
0.002572	115.6									
0.002548	119.4					22.3	30.19			
0.002547	119.6				14.60					
0.002545	120		6.69	13.3				33.5		
0.002542	120.5								43.0	
0.002512	125		11.1	20.8	23.35			52.0		
0.00251	125.5								79.0	
0.002512	125.05					41.3	49.92			
0.002482	130		17.5	31.0				80.0		
0.00248	130.3				39.40	53.6	83.55			
0.002478	130.5								102.0	98.0
0.002452	134.9					99.65	123.4			
0.00245	135		27.6	52.9						
0.002448	135.6				55.80					
0.002422	139.6					117.3				
0.00242	140	5.5	45.5	96.0						
0.002418	140.6				87.0					
0.002392	145	9.7								
0.002362	150	17.5								
0.002342	153.8	24.5								
0.002308	160	35.1								

* In these series the initial concentration of sulfur was 12.5 m moles.

about the least enhancement in the rate (Curve 8), that it makes almost no difference if natural rubber is vulcanized in the presence of DPG (diphenylguanidine) with or without zinc oxide (Curves 6 and 7), that sulfur in the presence of DPG reacts considerably faster in Perbunan than in natural rubber (Curve 3 and Curves 6 and 7), and that practically identical constants for the rate of sulfur disappearance are found when Perbunan is vulcanized in the presence of CMBTS or of an equimolar mixture of MBT and cyclohexylamine (Curves 1 and 2).

If the temperature function of the rate constant is plotted as carefully as possible—Table II provides the values for this—and if the apparent activation energy is calculated from the slopes of the curves, it is found that this value is about 35 kcal/mole for the reaction between sulfur and natural rubber, but for accelerated vulcanizations the value is between 28 and 30 kcal/mole. Thus it is seen that the accelerators—regardless of their special nature—effect a lowering of about 6 kcal/mole in the activation energy.

EXPLANATION OF THE KINETICS OF DECREASE IN SULFUR CONCENTRATION IN ACCELERATED VULCANIZATIONS

From the statements made in the preceding section, it appears that also in accelerated vulcanizations there is a lack of agreement between the time law and the dependence on concentration of the rate of sulfur decrease and that it is different from what is given in the section concerning the reaction of rubber with sulfur (with no other additives). While it is true in the latter case that the time law and the dependence on concentration of the rate of sulfur decrease showed quite different exponents, yet valid laws for the chemical kinetics could be written for a large range of concentrations and reaction times, and this perhaps holds true for the time law in accelerated vulcanizations, but here there is—as will be shown—perhaps only an approximation. It may be that the time law in accelerated vulcanizations has significance only as an interpolation formula, which can serve only for determining the sulfur transformed in the definite times as well as the initial rate of sulfur decrease; it says but little, if anything, about the nature of the decrease of the sulfur Consideration of the characteristics of the kinetics of sulfur decrease given in the previous section shows that the dependence of the initial rate on concentration, neither for constant sulfur concentration with varying accelerator content nor for constant accelerator content with varying sulfur concentration, can be expressed by a power law, that is to say, the dependence of the rate on concentration in general yields no reaction order in the usual sense.

The dependence of the initial rate of sulfur decrease upon the initial concentration of reactants (sulfur and accelerator), which is frequently found and which is given schematically in Figures 1 and 2, is now frequently noted in the kinetics of catalysis by intermediate compounds, especially in enzyme reactions[12]. The course of the curves in Figures 1 and 2 is explained by assuming that an equilibrium is established between the reactants, the catalyst and an intermediate compound formed from the two, which reacts further indirectly or directly. It is then assumed that the equilibrium is either established faster than the secondary reaction of the intermediate compound, or that both processes go with about the same speed.

Applying these ideas to the data pertaining to accelerated vulcanizations, we would have to assume the validity of the reactions as defined by Equations

(9) and (10) (B = accelerator, ZV = intermediate compound,

Vu = vulcanizate and Ka = rubber)

or

$$B + S_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ZV \text{ (fast)} \tag{9}$$

$$ZV + Ka \xrightarrow{k_2} Vu \text{ (slower and time determining)} \tag{10}$$

We can now, following the explanation by Laidler[13], find a statement for the rate of formation of the end product, the vulcanizate, by computing the concentration of the intermediate compound by using the equilibrium Equation (9), and putting the value into the expression which defines the rate of formation of the vulcanizate. Now since the reduction in concentration of sulfur, with which we are here concerned and which we measure, correponds to the reaction of the intermediate compound, we have

$$-d(ZV)/dt = -d(S_8)dt = k_2(ZV)(Ka) \tag{11}$$

From Equation (9) we first get Equation (12), and then using $(S_8)_0$ and $(B)_0$ for initial concentrations of sulfur and accelerators, we get Equation (13).

$$\frac{ZV}{(S_8)(B)} = K \tag{12}$$

$$\frac{(ZV)}{[(S_8)_0 - (ZV)][(B)_0 - (ZV)]} = K \tag{13}$$

This latter equation is quadratic in ZV; hence it is customary and appropriate to consider the relations in cases when either sulfur or accelerator is in excess concentration. Thus, when $(S_8)_0 \gg (B)_0$, we have:

$$\frac{(ZV)}{[(S_8)_0 - [(B)_0 - (ZV)]} = K \tag{14}$$

and for $(B)_0 \gg (S_8)_0$:

$$\frac{(ZV)}{[(S_8)_0 - (ZV)](B)_0} = K \tag{15}$$

From Equations (14) and (15), which are now linear in ZV, we get the value of ZV when $(S_8)_0 \gg (B)_0$ and $(B)_0 = \text{const}$, thus:

$$(ZV) = \frac{(B)_0 - (S_8)_0}{(S_8)_0 + 1/K} \tag{16}$$

or when $(B)_0 \gg (S_8)_0$ and $(S_8)_0 = \text{Const.}$

$$(ZV) = \frac{(B)_0(S_8)_0}{(B)_0 + 1/K} \tag{17}$$

If the expressions for (ZV) from Equations (16) and (17) are introduced into Equation (11) we get Equations (18) and (19) which give the decrease in concentration of the intermediate compound as well as of the sulfur:

$$-\left[d(\mathrm{ZV})/dt\right]_0 = -\left[d(\mathrm{S_8})/dt\right]_0 = \frac{k_2(\mathrm{B})_0(\mathrm{S_8})_0(\mathrm{Ka})}{(\mathrm{S_8})_0 + 1/K} \tag{18}$$

$$-\left[d(\mathrm{ZV})/dt\right]_0 = -\left[d(\mathrm{S_8})_0/dt\right]_0 = \frac{k_2(\mathrm{B})_0(\mathrm{S_8})_0(\mathrm{Ka})}{(\mathrm{B})_0 + 1/K} \tag{19}$$

The dependence of the initial rate of sulfur decrease upon the initial concentration of sulfur with constant accelerator concentration, as shown in Equation (18), and upon the accelerator concentration with constant sulfur concentration, as shown in Equation (19), will be determined essentially by the relative magnitude of the two terms of the sum in the denominator.

The greater the value of K and hence the smaller $1/K$, the sooner can $1/K$ be neglected in comparison with $(\mathrm{S_8})_0$, for example, in Equation (18) with increasing sulfur concentration $1/K$ becomes negligible compared to $(\mathrm{S_8})_0$, so the value of $(\mathrm{S_8})_0$ cancels and the initial rate becomes constant. Likewise, when in Equation (19), $1/K$ becomes negligible compared to $(\mathrm{B})_0$, and $(\mathrm{B})_0$ cancels, then the initial rate becomes independent of the accelerator concentration, and thus becomes constant. On the other hand, if the initial concentrations of sulfur or of accelerator in Equations (18) or (19) become very small so that finally they may be neglected compared with $1/K$, then the initial rate of sulfur decrease must rise linearly either with the sulfur concentration (when accelerator is constant) or with the accelerator concentration (when sulfur is constant). Naturally there are shadings between these extreme cases. We know that the general shape of the curves to be expected correponds to what has been repeatedly observed by us for accelerated vulcanizations (see previous Section).

It must be admitted that the expression of the results by Equations (18) and (19) has, for the present, only a formal character. If we take the vulcanizations which are accelerated with organic bases, for example, we must say: if—according to the ideas of Krebs[14]—we may assume that the bases react with sulfur to produce compounds with betaine-like structures which contain the sulfur in chainlike molecules which increase its reactivity, and that these compounds can form as intermediate compounds during vulcanization, we must nevertheless consider the fact that at present no details are known about the existence of a true equilibrium between sulfur, base and amine-polysulfide under the conditions found during vulcanization, just as we know nothing about stoichiometric relations for the reactions which are given schematically according to Equation (9). Finally, we are not sufficiently well informed about the role of side reactions which may well enough take place in these cases. However, there will be much in favor of the explanation we have developed of accelerated vulcanization being a catalysis by intermediate compounds, if in the following, we can show that right good agreement between theory and experiment is obtained by appropriate treatment of the data with Equations (18) and (19). From this, it seems to us that the fundamental idea, upon which the previously disclosed concepts are based, can prove correct.

When we write the reciprocals of Equations (18) and (19) we readily have:

$$1/[d(S_8)/dt]_0 = \frac{1}{k_2K(S_8)_0(B)_0(Ka)} + \frac{1}{k_2(B)_0(Ka)} \tag{20}$$

$$1/[d(S_8)/dt]_0 = \frac{1}{k_2K(S_8)_0(B)_0(Ka)} + \frac{1}{k_2(S_8)_0(Ka)} \quad . \tag{21}$$

Equation (20) signifies that the reciprocal of initial rate of sulfur decrease will be a linear function of the reciprocal of the initial sulfur concentration, if the accelerator content is held constant; likewise, according to Equation (21), it will be a linear function of the reciprocal of the initial accelerator content, when the sulfur content is held constant.

Another evaluation, which is similar to the preceding, is obtained when we write the following for Equations (18) and (19):

$$\frac{[d(S_8)/dt]_0}{K} + (d(S_8)/dt)_0(S_8)_0 = k_2(S_8)_0(B)_0(Ka)$$

$$\frac{[d(S_8)/dt]}{K} + (d(S_8)/dt)_0(B)_0 = k_2(S_8)_0(B)_0(Ka)$$

Transformation of these gives Equations (22) and (23)

$$\frac{[d(S_8)/dt]_0}{(S_8)_0} = k_2K(B)_0(Ka) - K[d(S_8)/dt]_0 \tag{22}$$

$$\frac{[d(S_8)/dt]_0}{(B)_0} = k_2K(S_8)_0(Ka) - K[d(S_8)/dt]_0 \tag{23}$$

According to these equations, we will get straight lines if the quotients of the initial rate of sulfur decrease over the initial sulfur concentration (when accelerator content is constant), or over the initial accelerator content (with constant sulfur), are plotted against the initial rate of sulfur decrease. Thus we can obtain the value for the equilibrium constant assumed from Equation (9), directly from the slope of the lines, while the rate constant in Equation

TABLE III

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF PERBUNAN BY SULFUR WITH CMBTS AT 115° C (ACCELERATOR CONTENT CONSTANT AT 10 M MOLES; SULFUR CONCENTRATION VARIED) (SCHEELE, TOUSAINT, AND CHAI)

$(S_8)_0$ m moles/100 g	$\frac{1}{(S_8)_0}$	$k' \cdot 10^3$ $(n = 0.8)$	$\frac{[d(S_8)/dt]_0}{=k' \cdot (S_8)_0^{0.8}}$	$\frac{1}{[d(S_8)/dt]_0}$	$\frac{[d(S_8)/dt]_0 \cdot 10^3}{(S_8)_0}$
5	0.2	37.5	0.136	7.35	27.2
5.72	0.175	33.0	0.133	7.52	23.5
6.67	0.15	31.0	0.141	7.1	21.3
8.0	0.125	29.0	0.153	6.54	19.1
10.0	0.1	24.5	0.155	6.45	15.5
13.33	0.075	23.0	0.133	5.46	13.8
20	0.05	18.5	0.203	4.93	10.1
30	0.033	15.0	0.228	4.39	7.6

TABLE IV

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF PERBUNAN BY SULFUR WITH DPG AT 130° C (DPG CONSTANT AT 10 M MOLES; SULFUR CONCENTRATION VARIED) (SCHEELE AND REDETZKY)

$(S_8)_0$ [m moles/100 g]	$\frac{1}{(S_8)_0}$	$k' \cdot 10^3$ $(n = 0.8)$	$[d(S_8)/dt] \cdot 10^3 = k' \cdot (S_8)_0^{0.8}$	$\frac{1}{[d(S_8)/dt]_0}$	$\frac{[d(S_8)/dt]_0 \cdot 10^3}{(S_8)_0}$
5	0.2000	109.6	397.2	2.52	79
10	0.1000	89.0	561.6	1.78	56
15	0.0666	77.2	673.7	1.48	45
20	0.0500	63.0	692.1	1.44	35
25	0.0400	56.7	744.6	1.34	30
30	0.0333	50.6	768.9	1.30	26
35	0.0286	43.5	747.7	1.34	21

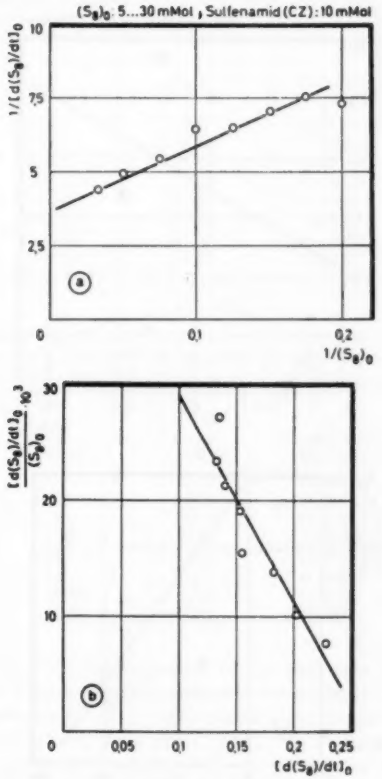

FIG. 4(a) and (b).—Concentration dependence of the rate of sulfur decrease, according to Equations (20) and (22), for the vulcanization of Perbunan at 115° C in the presence of CMBTS. (accelerator content constant [10 m moles]; sulfur varied). Ordinate and Abecissa: as given.

TABLE V

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH DPG AT 140° C (SULFUR CONSTANT AT 10 M MOLES; ACCELERATOR VARIED) (CHERUBIM AND SCHEELE)

(DPG) [m moles/100 g]	$\frac{1}{(DPG)_0}$	$k' \cdot 10^3$ ($n = 0.7$)	$[d(S_8)/dt]_0 = k' \cdot (S_8)_0^{0.7}$	$\frac{1}{[d(S_8)/dt]_0}$
2.0	0.500	14.0	0.070	14.3
3.5	0.286	24.0	0.120	8.34
5.0	0.200	42.5	0.210	4.72
7.5	0.138	73.0	0.366	2.74
10.0	0.100	95.0	0.485	2.10
15.0	0.067	125	0.625	1.60
20.0	0.050	138	0.690	1.45
30.0	0.033	150	0.750	1.33
40.0	0.025	150	0.780	1.33

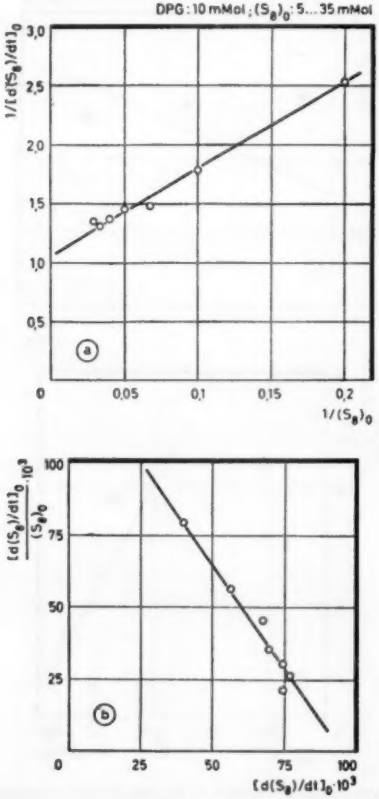

FIG. 5(a) and (b).—Concentration dependence of the rate of sulfur decrease according to Equations (20) and (22), for the vulcanization of Perbunan at 130° C in the presence of DPG (accelerator content constant at 10 m moles; sulfur varied). Ordinate and Abscissa: as given.

TABLE VI

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH DPG AT 115° C (SULFUR CONSTANT AT 10 M MOLES S_8; ACCELERATOR VARIED) (SCHEELE AND CHERUBIM)

(DPG) [%]	$\frac{1}{(DPG)_0}$	$k' \cdot 10^3$ ($n = 0.7$)	$\frac{d(S_8)/dt}{= k' \cdot (S_8)_0^{0.7}}$	$\frac{1}{[d(S_8)/dt]_0}$
0.5	2.0	1.75	0.00876	114
1.0	1.0	4.25	0.0213	46.9
1.5	0.667	6.75	0.0338	29.6
3.0	0.333	11.1	0.0556	18.0
4.0	0.25	12.0	0.0602	16.6
5.0	0.2	12.5	0.0626	15.98
6.0	0.1668	12.2	0.0612	16.38

TABLE VII

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH DPG AND ZnO AT 155° C (ZnO CONTENT AND SULFUR CONCENTRATION CONSTANT AT 10 M MOLES; ACCELERATOR CONTENT VARIED) (SCHEELE AND SCHAPER)

$(DPG)_0$ [m moles/ 100 g]	$\frac{1}{(DPG)_0}$	$k' \cdot 10^3$ ($n = 0.8$)	$\frac{[d(S_8)/dt]_0}{= k' \cdot (S_8)_0^{0.8}}$	$\frac{1}{[d(S_8)/dt]_0}$
2.5	0.40	2.27	0.01434	69.70
5.0	0.20	4.20	0.02650	37.70
10.0	0.10	9.70	0.06120	16.32
15.0	0.0667	13.13	0.08284	12.07
20.0	0.0500	16.05	0.1013	9.86
30.0	0.0333	18.20	0.1148	8.71
40.0	0.0250	18.20	0.1148	8.71
50.0	0.0200	17.53	0.1107	9.03

TABLE VIII

DEPENDENCE ON CONCENTRATION OF THE RATE OF DECREASE OF SULFUR IN THE VULCANIZATION OF NATURAL RUBBER BY SULFUR WITH ANILINE AT 140° C (SULFUR CONCENTRATION CONSTANT AT 10 M MOLES; ACCELERATOR VARIED) (CHERUBIM AND SCHEELE)

$(Aniline)_0$ [m moles/ 100 g]	$\frac{1}{(Aniline)_0}$	$k' \cdot 10^3$ ($n = 0.7$)	$\frac{d(S_8)/dt}{= k' \cdot (S_8)_0^{0.7}}$	$\frac{1}{[d(S_8)/dt]_0}$
1.0	1.0	6.2	0.031	32.2
2.5	0.40	8.2	0.041	24.4
3.5	0.286	9.1	0.0452	22.2
5.0	0.20	11.6	0.0582	17.2
10.0	0.10	14.9	0.0746	13.4
20.0	0.05	16.5	0.0826	12.1
30.0	0.0333	17.3	0.0866	11.55
40.0	0.025	19.0	0.0952	10.5

(11) can be deduced from the intercept of the ordinate, provided the rubber concentration as well as the initial concentration of sulfur and of accelerator are known and the value for K is ascertained from the slope.

In Tables III to VIII, we show the dependence on concentration of the rate of sulfur decrease for several accelerated vulcanizations which we have thus far carefully studied. DPG, aniline and CMBTS were the accelerators, and Perbunan and natural rubber were the elastomers. It should be noted in dealing with the values listed, that sulfur concentration is given in all cases in m moles S_8 per 100 grams rubber compound, and time is in minutes in all cases.

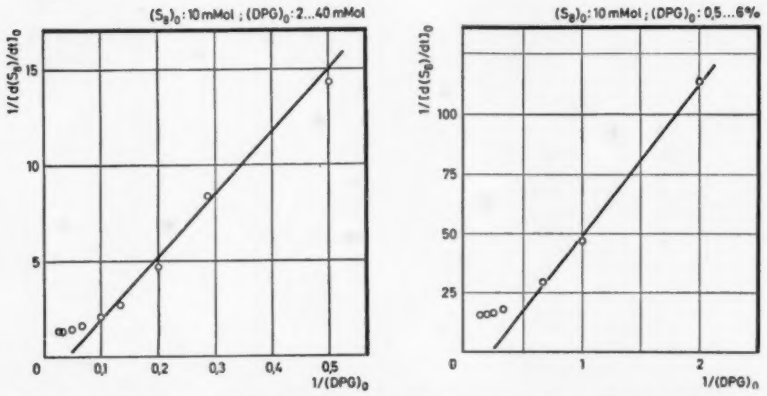

FIG. 6.—Concentration-dependence of the rate of sulfur decrease, according to Equation (21), for the vulcanization of natural rubber in the presence of DPG at 140° C (sulfur concentration constant at 10 m moles S_8; accelerator content varied). Ordinate and Abscissa: as given.

FIG. 7.—Concentration-dependence of the rate of sulfur decrease, according to Equation (21), for the vulcanization of natural rubber in the presence of DPG at 115° C (sulfur concentration constant at 10 m moles S_8; accelerator content varied). Ordinate and Abscissa: as given.

Figures 4a and 4b as well as 5a and 5b should demonstrate that in vulcanization of Perbunan under conditions of increasing initial concentration of sulfur with constant accelerator content (CMBTS or DPG), we get straight lines with good accuracy by presentation of the research data according to Equations (20) and (22).

Then too, when we keep the sulfur concentration constant and vary the accelerator content, we get straight lines if we comply with Equation (21), by plotting the reciprocal of the initial rate of sulfur decrease against the reciprocal of the initial accelerator concentration. This is shown in Figures 6 to 9. Therein are shown data on vulcanization of natural rubber by sulfur with in-

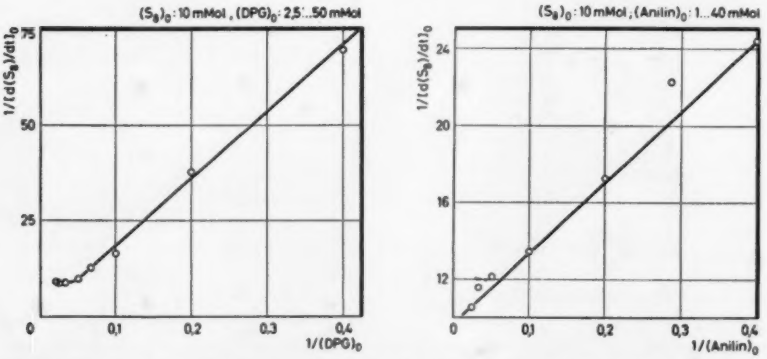

FIG. 8.—Concentration-dependence of the rate of sulfur decrease, according to Equation (21), for the vulcanization of natural rubber in the presence of diphenylguanidine and zinc oxide at 115° C (sulfur concentration constant at 10 m moles S_8; accelerator content varied). Ordinate and Abscissa: as given.

FIG. 9.—Concentration dependence of the rate of sulfur decrease, according to Equation (21), for the vulcanization of natural rubber in the presence of aniline at 140° C (sulfur concentration constant at 10 m moles S_8; accelerator varied). Ordinate and Abscissa: as given.

creasing amounts of DPG, at 140° and 115° (Figures 6 and 7) with increasing DPG in the presence of zinc oxide (constant) at 115° (Figure 8) and with increasing aniline concentration at 140° (Figure 9).

In complex reactions—and we must certainly consider accelerated vulcanization as such—we can derive a kinetic mechanism which reveals the true character of a reaction, only from results of studies in narrow ranges of reaction, and as in such cases, so it happens here, that the concentration—dependence of the rate of sulfur decrease must provide the deciding criterion. Nevertheless, we can investigate what may be expected, after the preceding explanations, with regard to the change of sulfur concentration with time. Information concerning this may be gained by integration, for example of Equation (18).

Without going into details, it seems from the expression that is thus derived, that the reduction in sulfur concentration fulfills a 1st order time law in the range of very low sulfur concentrations, that exponents ranging between 1 and 0 are noted for the time law for medium sulfur concentrations, and with very high sulfur concentrations at the start of the reaction, ranges of constant rate of sulfur decrease are found. Now of course we may not expect complete agreement in what happens kinetically in this case with respect to time and concentration, for we must assume some effect by the reaction product on the rate of decrease of sulfur also in accelerated vulcanizations; in other words, the autocatalytic nature of the decrease in sulfur can blur the results. After all, it seems to us, we must observe that the exponent of the time law changes not only with the course of an arbitrary reaction curve, but also with the initial concentration of the sulfur, which signifies that there must be a dependence on concentration of the exponent of the time law. However, the fact that experiment in every case yields exponents of the time law which are good over a wide range and also independent of temperature and concentration, presents us with a situation which seems impossible to clarify in the present state of things, for the relations here cannot be ignored.

Kinetic studies and their results do not always provide the key to complete understanding of a chemical reaction. That is well known to every worker in kinetics and urges caution whenever we feel inclined to draw any detailed conclusions. This holds true for the kinetics of vulcanization.

As previously mentioned, according to Krebs[14], organic bases and sulfur, for example, should come to equilibrium with the formation of a betain-like aminepolysulfide, and the assumption is made that this kind of equilibrium is established in a vulcanization which is accelerated by bases. However, we must keep clearly in mind the following state of affairs; even though we can explain the characteristic course of the initial rate of sulfur decrease with the concentration of reactants as is illustrated in Figures 1 and 2, by introducing a general equilibrium, formulated according to Equation (9), between sulfur, accelerator and intermediate compound, yet we must not in any way see in this agreement between the theory and experimental results, a proof of the existence of the equilibrium; it is much better to say that the kinetic results make the existence of some such equilibrium seem probable.

In view of this state of affairs, based on the character of the kinetics, the question arises, if the course of the initial rate of sulfur decrease with the concentration of reactants as given schematically in Figures 1 and 2, or more particularly, if the constancy of the rate that finally shows up at higher concentrations, can have some other reason.

Solubility relations may be suggested in helping to answer the question. Thus, the constancy of initial rate of sulfur decrease (accelerator constant) in

the range of higher sulfur concentrations, may result from the fact that the concentration of free sulfur prescribed by the equilibrium given in Equation (9), because of the continually rising initial concentration, finally reaches and passes the saturation concentration, so that the initial rate can increase no further. Thus, we have the case that the independence of the initial rate on the concentration, where there is catalysis by intermediate compounds, is not determined by the limitations of the proposed equilibrium, but rather appears prematurely as the result of the limited solubility of reactants.

Actually, it would be very difficult in every case to decide what really happens. With regard to the vulcanization reactions here discussed, the following items may be considered:

1) If the solubility relations of sulfur play an important part, we should expect the curves for the change with time of the sulfur concentration (reaction curves) to show a decrease of sulfur according to zero order in the initial range

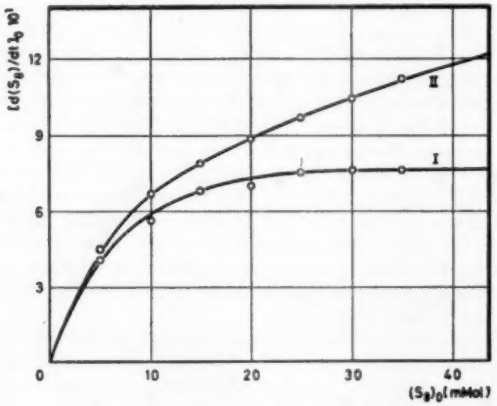

FIG. 10.—Dependence of initial rate of sulfur decrease upon the initial concentration of sulfur in the vulcanization of Perbunan at 130° C in the presence of 10 m moles (Curve I) and 50 m moles (Curve II) of DPG. Ordinate and Abscissa: as given.

of the reaction, either with or without autocatalysis (concave curves or linear concentration decrease). No certain support was found for this.

2) If exceeding the saturation concentration is the reason for constancy of the rate, we should expect it to occur suddenly, so that the rate would not gradually approach an end value, as is found by experience.

Figure 10 may help to illustrate what is said in 2) above. There the initial rate of sulfur decrease is plotted against the initial concentration of sulfur for vulcanizations of Perbunan with diphenylguanidine as accelerator. The work was done at 130° C. In each case, with increasing sulfur concentration, the DPG content was held at 10 m moles (Curve I) or at 50 m moles (Curve II) in 100 g of rubber compound. Curve I shows that the initial rate becomes practically constant when about 30 m moles of S_8 are present. Now if the reason for constancy of the initial rate lay in the fact that the sulfur exists, at the beginning of the reaction, as a solid phase in appreciable amounts whenever its initial concentration is 30 m moles/100 g or greater, then we should expect that constancy of rate, whenever the DPG content exceeds 10 m moles, would appear

actually at some other, yet approximately the same, sulfur concentration. However, this requirement is not met by Curve II (50 m moles DPG). As can be seen, it climbs steadily higher in the range of concentrations which is under discussion and always lies above Curve I (10 m moles DPG). The final value of the initial rate is quite evidently reached at a much higher sulfur concentration. More important than this observation is the fact that the initial rate—as can be plainly seen—gradually approaches its limiting value (highest rate) along a continually curving arc and does not reach it suddenly at a break in the curve.

If, after what has been said above, we are not forced to correlate the constancy of initial rate of sulfur decrease which finally develops in these vulcanizations at higher initial concentrations of reactants, with the solubility of the reactants, we may point to the fact that there are vulcanization reactions in which the kinetics show quite certain indications of solubility effects. We will return to cases of this kind at a later time. Whatever may be the cause for the existence of the practically constant initial rates of decrease of sulfur at higher levels of concentration of reactants, we believe after all that we may decide from the kinetics of sulfur decrease, that the course of accelerated vulcanizations follows a catalysis by intermediate compounds; and we see an important support for this conception in the disagreement between the time law and the dependence on concentration of the rate of sulfur decrease.

We can conclude from the foregoing discourse that accelerated vulcanizations have a great many characteristics in common from a kinetic viewpoint, so that an interpretation of the kinetics which may apply to the great majority of them could be attempted. The fact that there is a certain uniformity in the kinetics of vulcanization, at least as long as sulfur is the vulcanizing agent, must be looked upon as a fortunate circumstance. However, this fact need not lead to the conception of corresponding uniformity in the physical properties of the vulcanizates which are formed. These can be quite different from case to case, depending upon the special chemical composition and the number of crosslinks. The kinetics of sulfur decrease which is considered here can have nothing to do with this latter, for to the kinetics the kind of sulfur bonding is immaterial, as long as the sulfur reacts by way of an intermediate compound. Things are quite different of course when we study directly the kinetics of the crosslinking reaction (for example, through the change of swelling with time of vulcanization) and correlate the results with those for sulfur decrease.

As a matter of fact, in that way we find relationships which are of value in explaining the manner of vulcanization of different rubbers, concerning which we will report on at a later time.

SUMMARY

The present discussion deals with the explanation and critical analysis of the kinetics of the decrease in concentration of sulfur in accelerated and unaccelerated vulcanizations of natural and synthetic rubber. A marked distinction is made between the time law and the dependence on concentration of the rate of decrease of sulfur, since there is lack of agreement between them, both in accelerated and unaccelerated vulcanizations, which indicates the complex nature of vulcanization.

In unaccelerated vulcanization, the sulfur concentration drops, at all temperatures and independent of the concentration, according to a time law with exponent $n = 0.6$. On the other hand, the dependence on concentration of

the initial rate of sulfur decrease proceeds according to a first order reaction. These relations make it seem probable that sulfur decrease involves a process which is catalyzed by reaction products.

In accelerated vulcanization, the reduction of concentration of sulfur also is expressed by a time law with the exponent $n < 1$, and this too is independent of temperature and concentration of reactants (sulfur and accelerator). However, the concentration dependence of the rate of sulfur decrease cannot be expressed by a power law, so that we find no order of reaction in the usual sense. We attempt to explain the characteristic trend of the initial rate of sulfur decrease with sulfur concentration at constant accelerator content, or with accelerator concentration at constant sulfur content, by assuming that the vulcanization takes place through intermediate compounds. The pertinent theoretical conceptions are disclosed and critically examined and the attempt is made to show the extent to which they may be brought into accord with the experimental data.

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RELATION OF STRUCTURE TO PROPERTIES IN POLYURETHANES. CROSSLINKING STUDIES *

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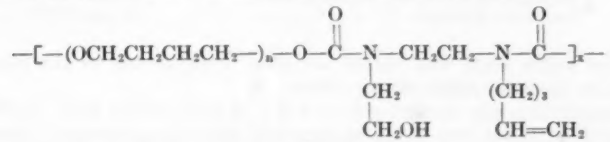
The present work was undertaken to assess the effect of crosslink structure on the properties of the elastic network derived from a linear polyetherurethane elastomer. In order to study this effect, a polyetherurethane was synthesized which contained two types of reactive sites suitable for establishing crosslinks—pendant hydroxyl groups for reaction with diisocyanate curatives and pendant double bonds for vulcanization with sulfur. Incorporation of both types of curing sites within the same linear polymer served to hold constant variables which might otherwise influence vulcanizate properties. Thus, the elastic networks formed by both curing systems were produced from the same polymer, and such factors as polymer molecular weight and molecular weight distribution, interchain forces and cure site distribution remained constant. Furthermore, the curing sites have been placed on pendant groups, well removed from the main polymer chain, in order to avoid degradation of the polymer by side reactions which may accompany sulfur vulcanization.

It is recognized that common elastomers with internal unsaturation, such as SBR and natural rubber, can be crosslinked by more than one method (e.g., with sulfur, peroxides, or high energy radiation), but the extent and nature of side reactions which may occur is not known with certainty. There are possibilities of polymer degradation reactions with all of these curing systems, and the occurrence of such degradation reactions would cloud any conclusions concerning the relation between crosslink structure and vulcanizate properties.

Polyetherurethane I was synthesized for the present study:



I

Reaction of the pendant hydroxyl groups with diisocyanates leads to the formation of bis-urethane crosslinks, and by proper choice of the diisocyanate curative, the length of the crosslink can be altered readily. Vulcanization through the pendant double bonds with accelerated sulfur systems leads to sulfur-containing crosslinks.

EXPERIMENTAL

Polytetramethyleneether glycol was synthesized by an acid-catalyzed polymerization of tetrahydrofuran[1]. The various samples used in this work had

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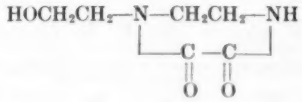
hydroxyl numbers ranging from 105.0 to 110.7 corresponding to molecular weights of 1068 to 1014. This glycol was stablized against oxidation by adding 1 weight per cent phenyl-2-naphthylamine.

N-(2-Hydroxyethyl)-N'-4-pentenylethylenediamine was prepared by alkylation of



with $CH_2{=}CH(CH_2)_3Br$, followed by hydrolysis. Details of this synthesis are to be reported elsewhere[2].

Polyetherurethane (*I*) was synthesized in an interfacial polycondensation reaction[3] by reacting the bis-chloroformate of polytetramethyleneether glycol with N-(2-hydroxyethyl)-N'-4-pentenylethylenediamine in chloroform solution with aqueous sodium carbonate as the acid acceptor. The average spacing of cure sites along the chain was approximately 1200 molecular weight units. Weight average (light scattering) and number average (osmotic) molecular weights were 195,000 and 54,000 respectively.

Curing of the elastomers was effected by three reagents:

a). 3,3'-Dimethoxy-4,4'-biphenylene diisocyanate (obtained from The Carwin Company, and purified by vacuum sublimation. Titration with di-n-butylamine indicated a purity of 98%).

b). The isocyanate-terminated polyetherurethane (molecular weight, approximately 5500) prepared by reacting 4 moles of polytetramethyleneether glycol and 5 moles of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate,

c). The accelerated sulfur recipe consisting of:

Sulfur	1.0 part PHR
Mercaptobenzthiazole disulfide	4.0 part PHR
Mercaptobenzthiazole	2.0 part PHR
Mercaptobenzthiazole disulfide·$ZnCl_2$	0.7 part PHR
Cadmium stearate	1.0 part PHR

When the sulfur level was varied the other constituents of the recipe were changed in the same relative proportion.

Compounding was carried out on a 2 × 6 inch rubber mill. Stocks were cured at 150° C for two hours in standard laboratory presses. Vulcanizate physical properties measured were: Yerzley resilience (ASTM-D945-52T), compression set (ASTM-D395-53T), Shore A hardness (ASTM-D676-49T) and modulus on the Instron tensile testing machine at a crosshead speed of 20 inches per minute.

Crosslink densities were calculated from modulus measurements carried out on samples swollen in toluene. Moduli were measured either in extension or compression[4]. Crosslink densities were computed from Equation 1:

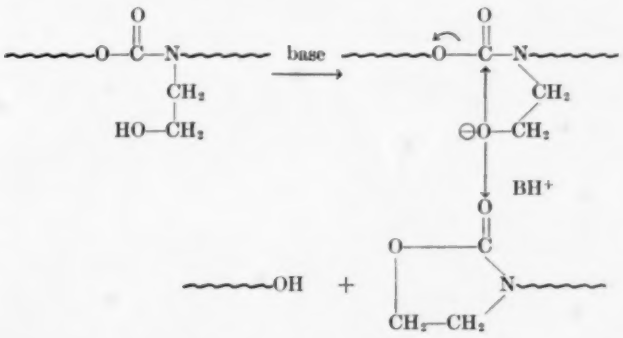
$$\nu_e/V = \frac{FV_r^{\frac{1}{3}}}{ART(\alpha - \bar{\alpha}^2)} \tag{1}$$

where ν_e/V represents the moles of effective network chains per ml of polymer,

F is the force in grams required to obtain an extension ratio of α, V_r is the volume fraction of elastomer in the swollen sample, A is the cross-sectional area of the unswollen sample, R is the gas constant and T is the absolute temperature. Equation 1 has been shown to be valid in systems where V_r is less than 0.25[5].

The sulfur crosslinks introduced by the curing system described above were characterized as follows: A reagent solution was prepared by dissolving 0.65 g of xylyl mercaptan in 130 ml of tetrahydrofuran and adding 1 ml of 0.5M benzyltrimethylammonium butoxide in t-butanol or 25% benzyltrimethylammonium hydroxide in methanol. Sulfur vulcanizates immersed in this solution dissolved on standing overnight at room temperature. The solutions were filtered to remove traces of insolubles and poured into a large excess of water to precipitate the solubilized polymers and to remove tetrahydrofuran. The recovered polymers were washed with additional water, dried on a mill at 100° C, and their intrinsic viscosities in a tetrahydrofuran-dimethylformamide mixture (86.2/13.8:wt/wt) were determined at 30° C.

Control experiments showed that diisocyanate vulcanizates of polyether-urethane I were insoluble in this basic mercaptan solution. However both the sulfur and diisocyanate vulcanizates dissolved in a tetrahydrofuran-quaternary ammonium base mixture which was free of mercaptan. Both of these vulcanizates contain unreacted hydroxyl groups so-located that a base-catalyzed cleavage of the urethane linkage is likely:



The fact that no high molecular weight polymer could be recovered from the solutions lends support to this hypothesis. Furthermore, a sulfur vulcanizate of a polyether elastomer, which was free of urethane linkages, was not solubilized by the solution of quaternary ammonium base in tetrahydrofuran although it did dissolve when mercaptan was present also.

Thioglycollic acid was an effective crosslink cleavage reagent also, although it was much slower in its action than xylyl mercaptan. Seven days were required for solution of the vulcanizates. Thioglycollic acid, however, has the advantage that it is more readily removed from recovered polymer by washing with water. Recovered polymer, redissolved in tetrahydrofuran, was crosslinked and insolubilized instantly upon addition of a small amount of iodine to the solution. Gelation occurred also if the solution was allowed to stand exposed to air for several hours. Results are summarized in Table I.

TABLE I

	Polyetherurethane I[1]-S vulc.		Polyetherurethane I[1]-DI cure		Polyether[2]	
	Behavior toward reagent	Characteristics of recovered polymer	Behavior toward reagent	Characteristics of recovered polymer	Behavior toward reagent	Characteristics of recovered polymer
Tetrahydrofuran Xylyl mercaptan Quat. am. base	Dissolved	$[\eta] = 1.70$	Insol.	—	Dissolved	$[\eta] = 1.54$
Tetrahydrofuran Thioglycollic acid Quat. am. base	Dissolved	Gelled in air	Insol.	—	Dissolved	Gelled in air
Tetrahydrofuran Quat. am. base	Dissolved	Low mol.wt.[3]	Dissolved	Low mol.wt.[3]	Insol.	—
Tetrahydrofuran	Insol.	—	Insol.	—	Insol.	—

[1] Intrinsic viscosity of uncured polymer = 1.24.
[2] Intrinsic viscosity of uncured polymer = 1.35. Polymer prepared from tetrahydrofuran, diethyloxetane and 2-(pentenoxymethyl)-2-methyloxetane by an acid catalyzed polymerization[4].
[3] A stable, milky suspension was formed when the solution was drowned in water in contrast to the other precipitations where the high molecular weight polymer coalesced.

DISCUSSION

A CROSSLINK STRUCTURE AND VULCANIZATE PROPERTIES

The concentration of effective network chains has been used as a parameter to correlate physical properties and crosslink structure. Concentration of effective network chains, rather than crosslink density, was used to avoid ambiguities which can arise in defining a crosslink once the network has been established. If the crosslinks are short, such ambiguities do not appear; there are two network chains per crosslink. However, in systems where long bifunctional molecules are used to crosslink a structurally similar linear polymer the relationship between the number of crosslinks and the number of network chains becomes obscure. It is then more convenient to use network chain concentration as the correlating parameter. If the molecule used to crosslink the linear polymer is long enough to exert an effect upon the equilibrium modulus, it will be counted properly as a network chain. If not, it will not be so counted.

The vulcanization of polyetherurethane I with 3,3′-dimethoxy-4,4′-biphenylene diisocyanate and accelerated sulfur systems provides crosslinks of different chemical structure. Reaction of the diisocyanates with the pendant

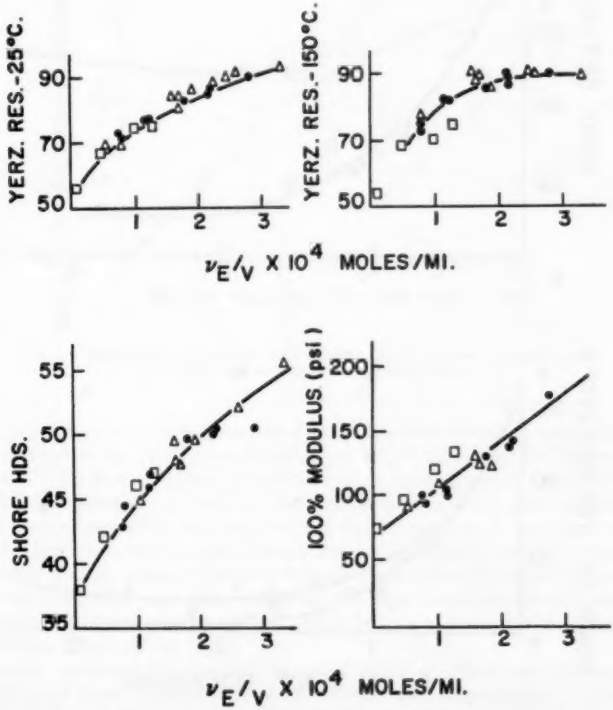


FIG. 1.—Dependence of resilience, modulus, and hardness on network chain concentration. (△) Vulcanization by sulfur, (○) by diisocyanate, (□) by isocyanate-terminated polyetherurethane.

hydroxyl groups produces urethane linkages, while sulfur vulcanization at the double bond gives a sulfur-containing bridge between pendant pentenyl groups. Use of a long chain, isocyanate-terminated polyurethane as the crosslinking agent introduces a segment which is about 19 times longer than that of the former diisocyanate reagent. In this case, the length of the crosslinking agent approaches the length of the network chains themselves.

Modulus, hardness and resilience (25° and 150° C) of the cured polyether-urethane I were found to be essentially independent of both the chemical nature and the chain length of the curing agent. Results are shown in Figure 1 where these properties are plotted as functions of effective network chain concentration.

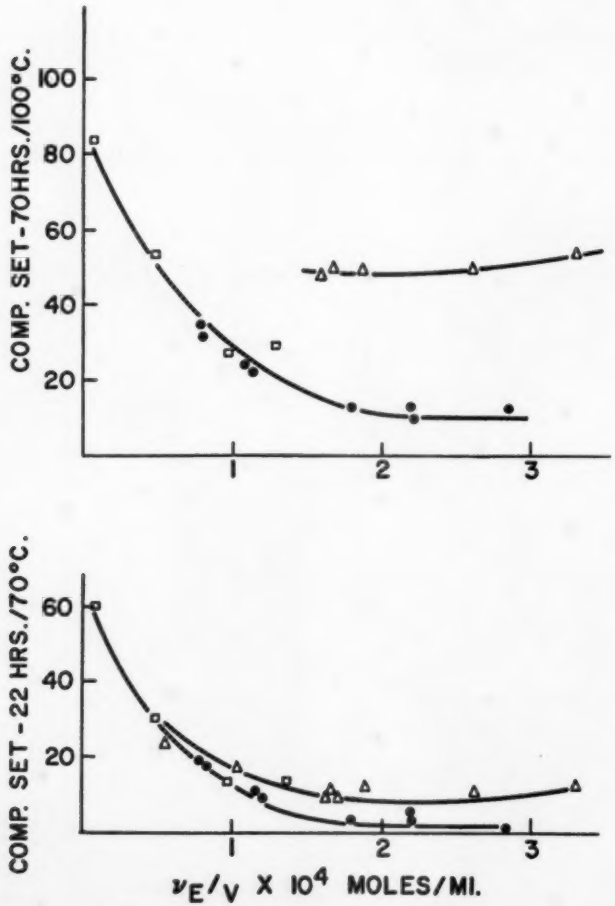


FIG. 2.—Dependence of compression set on network chain concentration. (△) Vulcanization by sulfur, (○) by diisocyanate, (□) by isocyanate-terminated polyetherurethane.

The results described above were obtained by tests which are non-destructive in nature. That is, the tests were either so short in duration or mild in nature that the specimen was essentially unchanged by subjection to the test. A more destructive test is the measurement of compression set, wherein the vulcanizate is subjected to high temperatures for relatively long periods of time, thus permitting chemical effects to come into play.

The response of the vulcanizates containing different crosslinks to the compression set conditions distinguished between the two chemically different types of crosslinks. In both tests (22 hrs. at 70° and 70 hrs. at 100°) the sulfur cures showed consistently higher compression sets than the diisocyanate cures at equivalent crosslinks densities (Figure 2). This difference was due, at least in part, to the thermal instability of the sulfur crosslink formed by the curing system utilized in this study. Both chemical and physical evidence is available to show that the sulfur crosslink consists predominantly of disulfides.

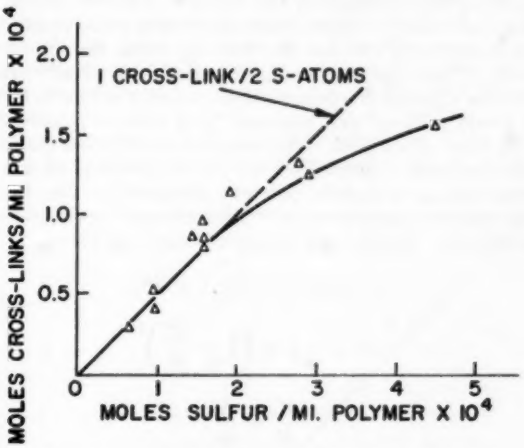


FIG. 3.—Dependence of crosslink concentration ($\frac{1}{2}\nu_0/V$) on sulfur concentration. Full line, experimental. Broken line, theory.

The physical evidence is shown in Figure 3, where crosslink concentration is plotted against moles of elemental sulfur per ml. of elastomer for the polyether-urethane I. Up to a crosslink concentration of approximately 1×10^{-4} moles/ml., which is equivalent to 24% of the double bond curing sites available, two moles of elemental sulfur are required for the formation of one mole of crosslinks. At higher sulfur usages, formation of a crosslink requires more than two moles of sulfur, possibly because the concentration of available cure sites is reduced to the point where the coupling reaction becomes less efficient. The data, however, do not rule out the possibility of a change in the curing mechanism at these high sulfur levels.

Chemical evidence for the formation of disulfide crosslinks is provided by the behavior of these vulcanizates when treated with mercaptans. Thus, when the vulcanizates are treated with either xylyl mercaptan or thioglycollic acid in basic tetrahydrofuran solution, they dissolve to form clear solutions from which

high molecular weight polymer can be recovered, and the recovered polymer is crosslinked readily by oxidation (see Experimental). These observations are consistent with the reaction scheme:

$$\text{(Polymer)—S—S—(Polymer)} \underset{I_2,\, O_2}{\overset{}{\rightleftharpoons}} 2\ \text{(Polymer) SH}$$

The higher compression set of the sulfur vulcanizates is attributable to the lability of the disulfide crosslinks. Application of stress at high temperatures induces rearrangement of the original disulfide crosslinks to relieve the applied stress. Similar behavior of disulfide linkages has been observed in other systems, particularly the polysulfide elastomers[7].

B) EQUATION OF STATE FOR RUBBERY ELASTICITY

In a polymer of infinite primary molecular weight the introduction of each crosslink results in the formation of two effective network chains. However, in crosslinking elastomers of finite molecular weight some chains are produced which are secured at only one end, the free end being the terminus of the primary molecule. This type of chain is not elastically effective in providing a restoring force for equilibrium deformations, since it is free to flow and relieve the imposed strain. Flory[8] and Scanlan[9] have derived relationships between the number of loose chain ends, total chains and effective chains. Scanlan's treatment also includes a correction for the sol fraction of the vulcanizate. The two treatments give slightly different relationships due to differences in weighting the relative importance of "trifunctional" crosslinks versus tetrafunctional crosslinks. Scanlan's relationship takes the form:

$$\nu_e = 2\rho(1 - S_1)^3(1 + 2S_1) \tag{2}$$

where

$$S_1 = -\tfrac{1}{2} + \left(\tfrac{1}{4} + \frac{M_c}{M}\right)^{\frac{1}{2}} \tag{3}$$

$$\frac{M_c}{M} = \frac{N}{2\rho} \tag{4}$$

and,

$$\nu_e \cong 2\rho\left(1 - \frac{M_c}{M}\right), \quad \text{for } M \gg M_e \tag{5}$$

ν_e is the number of elastically effective network chains, ρ is the total number of crosslinks, M_c is the molecular weight between crosslinks, M is the number average molecular weight and N is the number of original, uncrosslinked molecules.

Flory's treatment expressed in Scanlan's notation becomes:

$$\nu_e = 2\rho(1 - S_1)^3(1 + S_1) \tag{6}$$

and

$$\nu_e \cong 2\rho\left(1 - \frac{2\,M_c}{M}\right), \quad \text{for } M \gg M_e \tag{7}$$

Tests of the validity of the network-statistical theory of rubber elasticity require a method for measuring the degree of crosslinking. Thus, if the

efficiency of the crosslinking reaction can be determined, the effective network chain concentration for a polymer of known molecular weight can be computed from Equation 2 or 6. Flory, Rabjohn and Schaffer[5] used bis-azodicarboxylates as bifunctional coupling agents in natural rubber and obtained apparently good agreement between the statistical theory and the degree of crosslinking. However, the assumption that the coupling reaction was quantitative has been questioned by Moore and Watson[10]. The latter workers used di-*t*-butyl peroxide as the curing agent and determined the extent of crosslinking by analyzing the volatile decomposition products. The degree of crosslinking, as measured physically (Equation 1), was always greater than that measured chemically. The discrepency was ascribed to the presence of chain entanglements which acted as crosslinks.

In the present work, polyetherurethane I was crosslinked with 3,3′-dimethoxy-4,4′-biphenylene diisocyanate through its pendant hydroxyl groups. The isocyanate-hydroxyl reaction is known to produce urethanes in essentially quantitative yields in non-polymeric systems[11], and on the basis that this reaction retains its quantitative character in the polymer it offers a means for an additional test of the network equation. The diisocyanate curative was always the limiting reagent. Even at the highest state of cure only 40% of the available hydroxyls would have been utilized for complete reaction with the diisocyanate.

The chemical degree of crosslinking was calculated from the amount of diisocyanate used and the primary molecular weight (M_n = 54,000) by means

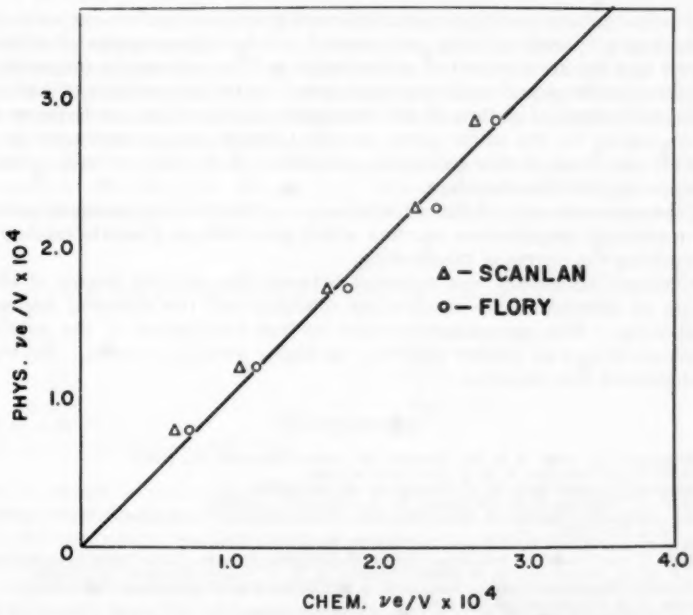


FIG. 4.—Comparison of physical and chemical values of degree of crosslinking for diisocyanate cures. Full line, theory, (○) Scanlan end correction, (△) Flory end correction.

of both Equations 2 and 6. The physical degree of crosslinking was determined from the equilibrium compression modulus of samples swollen in toluene by use of Equation 1. In all cases V_r was less than 0.25.

Physical values of ν_e/V as determined from equilbrium modulus measurements are plotted in Figure 4 against chemical values of ν_e/V claculated by both the Flory and Scanlan treatments (Equations 2 and 6). The sol correction is small and chemical values of ν_e/V calculated from Equations 5 and 7 give similar results. The solid line is that required by elastic theory. Both treatments give good agreement with theory and a choice between them is not possible on the basis of the present data. This agreement provides further verification of the network-statistical theory of rubbery elasticity in highly swollen systems ($V_r < 0.25$). That no chain entanglement was observed as in the case of Moore and Watson may be due to differences in primary molecular weight of the polymers used (54,000 in the present work vs. 250,000 for the natural rubber used by the English workers).

ACKNOWLEDGMENTS

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SYNOPSIS

A polyurethane bearing pendant hydroxyl groups and carbon-carbon double bonds was prepared. Curing was carried out by diisocyanates of different lengths and by an accelerated sulfur recipe. The vulcanizate properties of modulus, hardness and resilience were found to be independent of both the length and chemical nature of the crosslink. Compression set however was always higher for the sulfur cures, an effect which can be attributed to the disulfide structure of this particular crosslink. Both physical and chemical evidence support this structure.

Diisocyanate curing of the polyurethane via the hydroxyl groups is a clean-cut, essentially quantitative reaction which provided an absolute method for determining the degree of crosslinking.

Excellent agreement was obtained between the physical degree of crosslinking as determined by equilibrium modulus and the chemical degree of crosslinking. This agreement provides further verification of the network-statistical theory of rubber elasticity in highly swollen systems. No chain entanglement was observed.

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RELATION OF STRUCTURE TO PROPERTIES IN POLYURETHANES. EFFECT OF BRANCHING *

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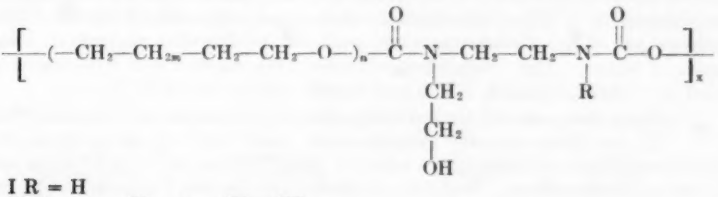
Correlation of the physical properties of elastomers with their molecular structure depends basically upon the availability of a systematic array of appropriate model polymers. Differences in molecular weight and its distribution, degree of linearity and structure and distribution of backbone constituents (in copolymers) among others are variables which can affect the physical properties of high polymers. In the classical vinyl polymerization systems control of these factors is at best, crude. However, the recently developed technology for the preparation of urethane block polymers provides the means for the reasonable control of structural details. The chemical reactions involved in the synthesis of polyurethanes are well defined and readily adaptable to the preparation of a variety of elastomers differing systematically in specific structural features. The necessary models for a detailed experimental correlation of physical properties with molecular structure are now a practical reality.

In the present work polyurethane technology has been used to investigate the effects of chain branching on polymer physical properties. Two aspects of chain branching phenomena have been examined: first, the influence of various short chain aromatic branches on the properties of polymers with fixed backbone structure and second, the influence of "loose ends", or long-chain branches, on polymer vulcanizate properties.

For the study of short chain branching polyether urethanes I and II were synthesized according to the method described previously[1]. Subsequent reaction of the pendant hydroxyl groups with various monoisocyanates pro-



I R = H
II R = —(—CH_2—)—$_2$ CH=CH_2

vided a means whereby short pendant chains of varying structure and in varying concentration could be attached to a high molecular weight, linear polyurethane backbone. The pendant double bonds in II provided cure sites for vulcanization with an accelerated sulfur recipe.

Long chain branching was studied in a series of polyether urethanes which were purposely branched in a controlled manner during the preparation. Con-

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densation of polytetramethyleneether glycol (molecular weight about 1000), trimethylolpropane and 2,4-hexadiene-1-ol with 2,4-toluene-diisocyanate provided branched polymers, the chain ends of which terminated in the 1,3-diene structure. Network formation (vulcanization) was effected by connecting the terminal diene functions through a Diels-Alder reaction with a bis-dieneophile, *m*-phenylenebismaleimide. The degree of vulcanization (or effective network chain concentration) was determined by the proportion of triol used in the polymer synthesis and by the number of chain ends connected by the curing agent. Long chain branches were introduced into the vulcanizates by using less than the stoichiometric amount of curative required to connect all the chain ends.

EXPERIMENTAL

The preparation of polyether urethane II, its curing by an accelerated sulfur recipe, and testing, and the measurement of effective network chain concentration have been described earlier[1]. Polyether urethane I was prepared in a similar manner from the bischloroformate of polytetra-methyleneether glycol (about 1000 molecular weight) and N-(2-hydroxyethyl) ethylenediamine (mole ratio = 1.00:1.03) and had an intrinsic viscosity of 1.05 at 30° C in a mixture of tetrahydrofuran and dimethylformamide (86.2/13.8:w/w). Both polymers contained pendant hydroxyl groups spaced about 1200 molecular weight units apart through which arylurethane groups could be attached by means of reaction with arylmonoisocyanates. In polyether urethane II, similarly spaced carbon-carbon double bonds were present also, and these served as sites for sulfur curing.

The reaction of monoisocyanates with the pendant hydroxyl groups of polyether urethanes I and II was carried out in the following manner. To a 22 weight per cent solution of polymer in purified tetrahydrofuran (distilled from lithium aluminum hydride) was added the requisite amount of isocyanate. The reaction was catalyzed with an equal weight mixture of ferric acetylacetonate and triethylamine, added as a one weight per cent solution in dry benzene. The concentration of catalysts in the reaction solution equalled 2.3×10^{-4} moles of ferric acetylacetonate and 6.6×10^{-4} moles of triethylamine for each mole of hydroxyl groups. After about 48 hours, the isocyanate concentration had dropped to 1–3% of its original value as determined by titration with dibutylamine. The solvent was removed by drowning the mixture in a large excess of water. The coagulated polymers were washed well with water and dried on a chrome-plated, 2 × 6 inch rubber mill at 105–110° C.

Crystallization rates of the several polymers were measured dilatometrically at 0° C. Solution viscosity measurements were made at 30° C in a tetrahydrofuran: dimethylformamide mixture (86.2/13.8:w/w) or in benzene using an Ostwald viscometer. Williams plasticity and recovery measurements were made at the specified temperatures according to ASTM test number D926-47T. Vulcanizate physical properties measured were: Yerzley resilience (ASTM D945-52T), compression set (ASTM D395-53T), temperature retraction (ASTM D1329-54T), and modulus on the Instron tensile testing machine[2] at a crosshead speed of 20 inches per minute.

The polyether urethanes used in the study of long chain branching were prepared in the following manner. To a homogeneous mixture of 2,4-hexadiene-1-ol, polytetramethyleneether glycol (about 1000 molecular weight) and trimethylolpropane was added a stoichiometric amount of 2,4-toluenediisocyanate

followed by 3 drops of 10% triethylamine solution in acetone and 6 drops of 5% ferric acetylacetonate solution in benzene per 100 m mole of diisocyanate. After a brief, vigorous stirring, the mixture became warm and was poured into an aluminum "toothpaste tube", sealed and heated for 16 hours at 80° C. The range of compositions studied varied from a triol/mono-ol mole ratio of 0.30 to 0.55 and a diol/mono-ol ratio of 4 to 12. Calculations indicate the gel point should be reached when the triol/mono-ol mole ratio = 0.33[3]. In practice it was found that soluble polymer was produced when this ratio was as high as 0.40–0.45. Compounding was carried out on a 2 × 6 inch rubber mill. Stocks were cured at 140° C for one hour in standard laboratory presses. In all cases, vulcanizate properties were determined on stocks cured with 1.3–3.3 PHR of *m*-phenylene bismaleimide and containing 30 PHR of HAF black.

RESULTS AND DISCUSSION

SHORT CHAIN BRANCHING

Short pendant chains of varying structure and in varying concentrations were attached to a high molecular weight, linear polyurethane backbone by reaction of various aryl monoisocyanates with the hydroxyl groups of polymers I and II to form pendant N-arylurethane structures. Use of this technique for the preparation of branched polymers held constant other variables which can affect physical properties such as molecular weight and its distribution, polymer backbone structure, distribution of the cure sites, nature of the crosslink, the environment in which the curing system operates, and the fraction of the polymer which is present as loose chain ends at any given state of cure.

These short pendant chains, or branches, were found to have a significant effect upon the rheological and solution properties of the raw polymer and upon the rate of crystallization of the polymer backbone. The basic vulcanizate properties of the polymeric backbone (in polyether urethane II), however, were not significantly changed.

The effect of branch concentration on crystallinity was studied by measuring crystallization rates of polymers containing different amounts of phenylurethane branches. For these experiments samples of the polyether urethane I were treated with phenylisocyanate sufficient to react with 50, 75, and 100% of the hydroxyl groups. Half lives for crystallization at 0° C are shown in Table I. The rate of crystallization was reduced considerably as the number

TABLE I

EFFECT OF BRANCH CONCENTRATION ON POLYMER PROPERTIES

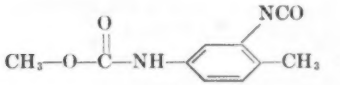
Phenylurethane branch concentration (moles/10^4 g)	Half-life of crystallization At 0° C (hrs)	Williams plasticity (30° C)	Williams recovery (30° C)
0.0	0.7	91	6
4.3	8.8	107	7
6.5	14.8	112	7
8.6	No Crystallization	121	9

of urethane branches increased. When 100% of the hydroxyl groups were substituted, no crystallization was observed at this temperature.

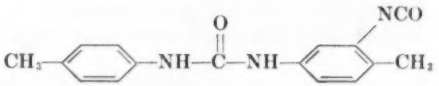
As indicated by the Williams plasticity values, shown in Table I, the polymers became increasingly viscous as the concentration of phenylurethane side

chains increased. Recovery values, also shown in Table 1, were altered only slightly, indicating that the interchain forces—presumably hydrogen bonding—responsible for the viscosity increase decayed relatively rapidly and did not contribute to elastic memory.

The effect of branch structure on physical properties was studied in polymers prepared by reaction of the hydroxyl groups in polyether urethane II with phenyl- and α-naphthyl-isocyanates, methyl N-(3-isocyanato-4-methylphenyl) urethane (III)[4], and N-(3-isocyanato-4-methylphenyl)-N′-*p*-tolylurea (IV). Only 90% of the stoichiometric amount of isocyanate was used. The resulting



III



IV

polymers contained, on the average, one arylurethane branch every 85 atoms along the chain.

Table II shows the effect of different N-arylurethane branches on plasticity and recovery. These measurements were made at both 30° C and 80° C. At both temperatures, the viscosity of the polymers increased as the estimated polarity of the aryl branch increased in the order: hydroxyl, monourethane, bisurethane, urethane-urea. At 30° C, the more polar branches, bisurethane and urethane-urea, caused relatively high recovery values as compared to the less polar hydroxyl and monourethane substituents. Thus, the more polar branches introduced interchain forces which persisted for a relatively long time. At 80° C, however, all recovery values were low, indicating a rapid decay of interchain forces. These observations are in accord with the idea that hydrogen bonding is in part, at least, the source of interchain forces in these polymers.

Solution viscosity variations caused by changes in the structure of the side chains are also shown in Table II. The intrinsic viscosities of the branched polymers show little variation with change in structure in the tetrahydrofuran-dimethylformamide solvent. This mixture is a very good one for polar molecules, and hence the viscosities are little affected by changes in the polar nature of the branch. However, in benzene an entirely different situation exists.

TABLE II

EFFECT OF BRANCH STRUCTURE ON POLYMER PROPERTIES

Structure of branch	Plasticity		Recovery		Intrinsic viscosity at 30° C	
	30° C	80° C	30° C	80° C	THF/DMF	Benzene
$-CH_2CH_2-OH$ (Control)	90	48	6	0	1.24	1.08
$-CH_2CH_2O\overset{O}{\overset{\|}{C}}NHC_{10}H_7$	108	53	6	1	1.14	1.17
$-CH_2CH_2O\overset{O}{\overset{\|}{C}}NHC_7H_6NH\overset{O}{\overset{\|}{C}}OCH_3$	158	69	38	1	1.15	0.90
$-CH_2CH_2O\overset{O}{\overset{\|}{C}}NHC_7H_6NH\overset{O}{\overset{\|}{C}}NHC_7H_7$	196	91	59	6	1.29	0.60

Intrinsic viscosities of polymers bearing highly polar branches (for example, the bisurethane or the urethane-urea) are lower than is the intrinsic viscosity of the parent polymer bearing hydroxyethyl side chains. This effect can be attributed to coiling of the polar molecules in a poor solvent.

These short chain branches had no major effect on the physical properties of gum vulcanizates measured over a wide range of crosslink density. Figure 1 shows Yerzley resilience (25°), 100% modulus, and compression set (22 hrs/70° C) as functions of crosslink density (expressed as moles of effective network chains per ml of polymer). Regardless of the branch structure—whether it be hydroxyl, monourethane or bisurethane—all the polymers exhibit essentially the same physical properties at equivalent states of cure. The intermolecular forces responsible for the increase in polymer bulk viscosity and elastic memory in the branched polymers are either not strong enough or are too limited in number to significantly alter these vulcanizate properties. In agreement with

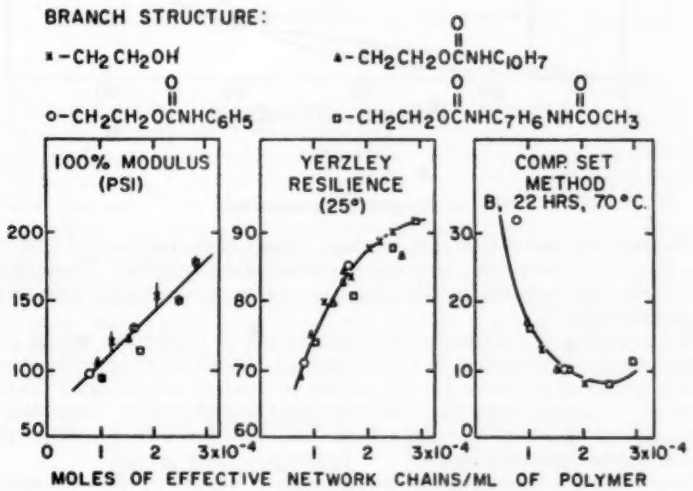


FIG. 1.

the crystallization rate phenomena observed in derivatives of polyether urethane I, the temperature retraction measurements recorded in Figure 2 demonstrate that T-50 values of sulfur-cured gum vulcanizates of polymers prepared from polyurethane II are greatly lowered by the presence of phenyl-and naphthylurethanoethyl branches. The two polymers with arylurethane side chains have T-50 values about 50° C lower than that of their parent polymer containing hydroxyethyl branches. The latter crystallizes either to a greater extent or more rapidly when cooled to −60° C, the temperature at which the retraction measurements are started. Retraction at low temperatures is limited to the small amount of amorphous material, and the crystalline segments must melt before further retraction can occur. The branched polymers on the other hand contain a larger proportion of amorphous material and therefore retract more at low temperatures before reaching the region where crystallinity must disappear for further retraction to occur.

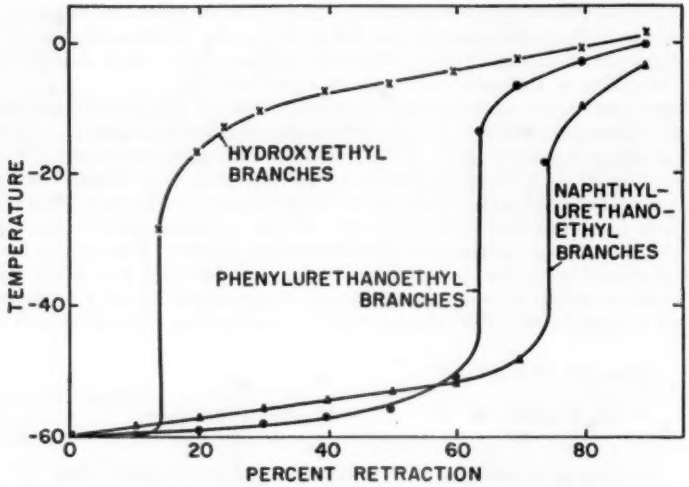


FIG. 2.

LONG CHAIN BRANCHING

The second phase of this work involved a study of the influence of long chain branching, or "loose-ends", on polymer vulcanizate properties. Here, in contrast to the previous results, long chain branching altered vulcanizate properties significantly.

Condensation of polytetramethyleneether glycol (molecular weight about 1000), trimethylolpropane, and 2,4-hexadiene-1-ol with 2,4-toluenediisocyanate provide branched polymers, the chain-ends of which terminated in a 1,3-diene structure. Network formation (vulcanization) was effected by connecting the terminal diene functions through a Diels-Alder reaction with a bisdieneophile, meta-phenylenebismaleimide.

This branched chain polyurethane system is unique in that the uncured polymers have cure sites located at every chain end. Reaction of these terminal cure sites with the bismaleimide curative produces the elastic network. Effective network chain concentration is determined by the proportion of trimethylolpropane used in the polymer synthesis and by the number of chain ends connected by the curing agent. For a polymer of given trimethylolpropane content, the concentration of long chain branches in the vulcanizate depends on the amount of bismaleimide curative used.

Figure 3 shows vulcanizate data obtained on one branched chain polyurethane cured with varying amounts of bismaleimide. The polyurethane contained 0.9×10^{-4} moles of branch points, that is, trimethylolpropane per gram of polymer. Modulus at 300% elongation, Yerzley resilience at 25° C, and compression set (22 hrs at 70° C) have been plotted against the amount of bismaleimide curing agent used, expressed as a percentage of the stoichiometric amount needed to couple all the chain ends. Optimum values of these various vulcanizate properties were attained at close to 100% of the stoichiometric amount of curative.

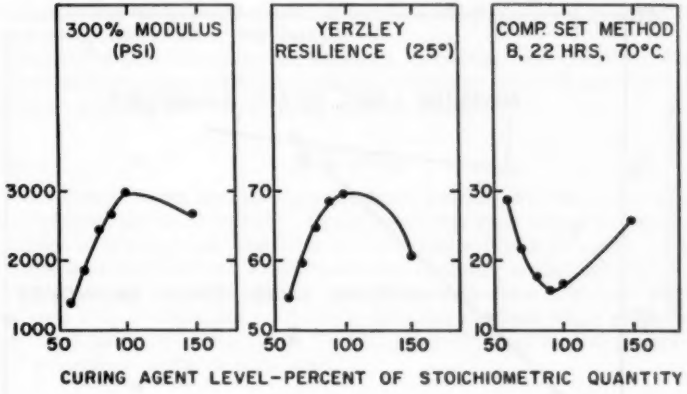


FIG. 3.

Modulus displays its expected behavior, on the basis that it is an index of the effective network chain concentration in this system. That is, as the amount of bismaleimide curative is increased—up to a point—more chain ends are connected and, consequently, effective network chain concentration and modulus increase. The maximum in the modulus curve indicates that cure site saturation is occurring in the presence of excess bismaleimide. That this maximum occurs at the theoretical usage of curative is evidence for the highly efficient nature of the Diels-Alder reaction in this system.

Figure 4 shows the effect of branch point concentration on modulus and compression set. In this series of polymers, effective network chain concentration was varied by changing the concentration of branch points in the raw polymers. All samples were cured with the stoichiometric amount of curing agent

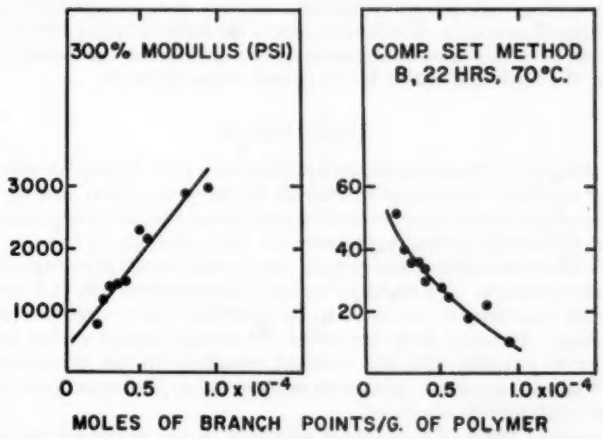


FIG. 4.

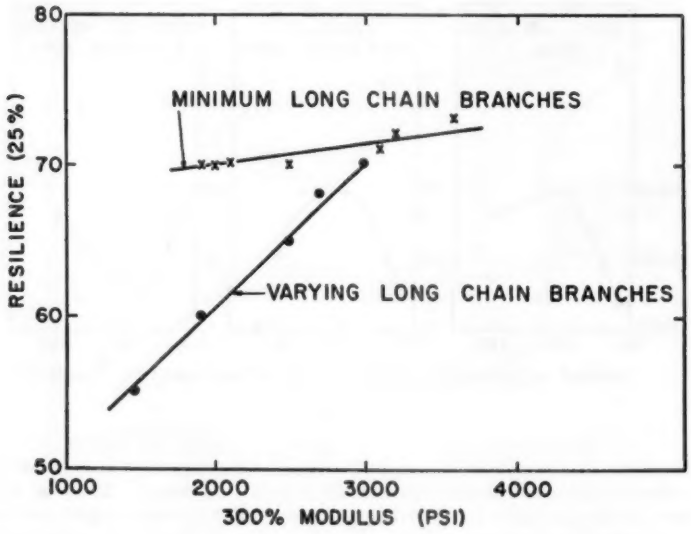


FIG. 5.

which minimized the concentration of "loose-ends". Modulus and compression set show the expected variations.

Figure 5 illustrates a significant feature of this polyurethane system. The resilience of vulcanizates in which "loose ends" are minimized is quite insensitive to the degree of vulcanization. In this graph resilience is plotted against the modulus which here is taken as a measure of the effective network chain concentration. When long chain branch (or "loose end") concentration was minimized by curing with the stoichiometric amount of *m*-phenylenebismaleimide, the resilience changed by only 3 units over a modulus range of 1500 to 3500 psi. In contrast, over this same modulus range in vulcanizates containing long chain branches, the resilience varied by 15 points—from 55 to 70.

CONCLUSION

Attaching short N-arylurethane branches to a high molecular weight, linear polyether urethane introduces interchain forces—very likely arising from hydrogen bonding—which increase as the side chains become more polar. These forces are sufficiently strong to increase the bulk viscosity of the raw polymers and, with the more highly polar groups, are strong enough to impart an appreciable elastic memory. At slightly elevated temperatures (80° C) these forces are reduced considerably, which is to be expected if they arise through hydrogen bonding. However they are either not strong enough or are too limited in number to compete with the covalent crosslinks in the elastomer vulcanizates. Thus no significant alteration is observed in the vulcanizate properties which are customarily measured.

The marked effect of these short aryl side chains to reduce crystallization tendencies can most likely be attributed to the bulkiness of the pendant aryl

moiety, which prevents—or slows down—the ordering of the polytetramethyleneether chains into a crystal lattice.

Long chain branches influence dynamic properties considerably. Present evidence indicates that optimum dynamic properties—as measured by Yerzley resilience—are obtained when "loose ends" are absent.

SYNOPSIS

The effect of short arylurethane branches on the physical properties of a linear polyurethane is described. Branches of this type reduce crystallization tendencies of the polymer and alter its bulk and solution viscosity behavior. Vulcanizate properties, such as resilience and modulus, are not affected.

The synthesis of polyurethanes containing long-chain branches with terminal cure sites is described. Dynamic behavior of these latter polymers, as judged by Yerzley resilience, improves as the proportion of long chain branches in the vulcanizate network is reduced.

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THE CHEMISTRY OF VULCANIZATION. VIII. ROLE OF ZINC BUTYRATE IN THE REACTION OF DIPHENYLMETHANE, SULFUR AND 2-BENZOTHIAZOLYL DISULFIDE *

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INTRODUCTION

Diphenylmethane (DPM) which contains α-methylenic hydrogen has been used as a model of rubber hydrocarbon, and reactions involving DPM, sulfur and thiazole type accelerators in the absence of zinc oxide or soap were reported in previous papers[1,2,3]. These papers reported that 2-mercaptobenzothiazole (MBT), 2-benzothiazolyl disulfide (MBTS)[2] and zinc salt of 2-mercaptobenzothiazole (ZMBT)[3] generate the same radical, i.e., 2-benzothiazolesulfenyl which has the accelerating effect. This radical opens the ring of elementary sulfur and thus accelerates vulcanization since the spontaneous splitting of the sulfur ring molecule to a biradical was found to be the rate determining step in the reaction of DPM with sulfur alone[4]. Processes by which accelerators generate this radical differ from each other owing to the types of accelerators, that is, mercaptan[1], disulfide[2] and zinc mercaptide[3] type. The previous paper[5] reported the reaction involving DPM, sulfur and MBT in the presence of zinc butyrate. According to this, MBT first reacts with zinc butyrate to form butyric acid and ZMBT, the latter then generating the effective benzothiazolesulfenyl radical. Thus, even in the presence of zinc soap, the essential mechanism of acceleration is the same as in the absence of zinc soap, though the process and rate for forming benzothiazolesulfenyl radical are different in the absence of zinc soap. In the present paper the reaction of DPM, sulfur and MBTS in the presence of zinc butyrate are reported. The reaction mechanism will be deduced from the experimental results obtained here and from conclusions obtained in the previous papers. The rate equation for MBTS consumption and equation for the accelerating efficiency for this accelerator are derived from the mechanism. The theoretical equations were examined by experiments.

EXPERIMENTAL

DPM[1], MBTS[2] and zinc butyrate[5] were prepared or purified as before. The procedures for conducting the reaction and for isolating, identifying and determining the individual products were quite similar to those of the preceding paper[5].

RESULTS AND DISCUSSION

The reaction products.—The results of the reaction involving DPM, sulfur, MBTS and zinc butyrate are indicated in Table I.

* Translated by J. T. from *J. Chem. Soc. Japan., Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*) 62, 1254 (1959).

TABLE I

THE REACTION OF DPM (200 MMOLES), MBTS (5 MMOLES), SULFUR (40 MILLIGRAM ATOMS) AND ZINC BUTYRATE (12.5 MMOLES) AT 160° C IN CO_2

Reaction time, hrs	Reaction products, mmoles					MBTS recovery, per cent**	$\left(\frac{PS+TBP}{ZnS+ZMBT+MBT/2}\right)$, per cent
	TBP*	PS*	ZMBT	MBT	ZnS		
5	1.71	0.95	3.89	trace	0.39	77.8	62.3
10	2.52	1.50	3.34	1.58	2.30	82.7	62.6
20	3.20	6.25	1.20	5.03	7.93	74.3	85.5

* TBP and PS represent thiobenzophenone and benzhydryl polysulfide, respectively.
** This means (ZMBT+MBT/2)/MBTS used.

TBP, PS, MBT and ZnS increased with reaction time. On the other hand, ZMBT decreased as the reaction proceeded. At an earlier stage of reaction it is noteworthy that yield of TBP predominates over that of PS, though at the later stage the reverse situation is observed. This phenomenon was also observed in the reaction involving DPM, S, MBT and zinc butyrate.

Mechanism of activation by zinc soap.—The reaction mechanism can be deduced from conclusions obtained in the previous papers, since the reaction products here are similar to those for the reactions already reported. In the reaction involving DPM, sulfur and MBTS, the first step of the reaction is a thermal dissociation of MBTS to benzothiazolesulfenyl radicals. It is considered that even in the presence of soap this step precedes the other steps.

$$MSSM \longrightarrow 2MS^{\cdot}, \tag{10}$$

where MSSM represents MBTS, and $MS^{\cdot}$ the benzothiazolyl radical. Therefore, MSH and MSZnSM, which will appear below, represent MBT and ZMBT respectively. The radical $MS^{\cdot}$ generated in Reaction 10 either cleaves sulfur molecule or dehydrogenates DPM as indicated in Reaction 11 and 4″.

$$MS^{\cdot} + S_8(\text{ring}) \longrightarrow MSS_8(\text{chain}) \longrightarrow MS^{\cdot} + {}^{\cdot}Sx^{\cdot} \tag{11}$$

$$MS^{\cdot} + Ph_2CH_2 \longrightarrow MSH + Ph_2CH^{\cdot} \tag{4''}$$

Reaction 11 shows the elementary step for the accelerating mechanism as in the previous papers. All the sulfur radicals are indicated by only one symbol, $^{\cdot}S_x^{\cdot}$, since various sulfur radicals are considered to be identical except for their chain lengths. MSH, which appears for the first time in Reaction 4″, reacts with zinc soap $(RCOO)_2Zn$ as reported in Part VII.

$$2MSH + (RCOO)_2Zn \longrightarrow MSZnSM + 2RCOOH \tag{17}$$

MSZnSM thus formed is decomposed to the radical $MS^{\cdot}$ by sulfur molecule as reported in Part VI and VII.

$$MSZnSM + S_8(\text{ring}) \longrightarrow 2MS^{\cdot} + ZnS_8(\text{chain}) \tag{14}$$

The radical $^{\cdot}S_x^{\cdot}$ produced in Reaction 11 induces decomposition of MSSM or MSZnSM as reported in Parts V and VII.

$$MSSM + {}^{\cdot}Sx^{\cdot} \longrightarrow 2MS^{\cdot} + {}^{\cdot}Sx^{\cdot} \tag{13}$$

$$MSZnSM + {}^{\cdot}Sx^{\cdot} \longrightarrow 2MS^{\cdot} + ZnSx \tag{16}$$

Zinc polysulfides, which are produced as ZnS_8 (chain) in Reaction 14 and as ZnS_x in Reaction 16, are assumed to be identical and symbolized as ZnSx. This decomposes to zinc sulfide and sulfur radical.

$$ZnSx \longrightarrow ZnS + {}^{\cdot}S - 1^{\cdot} \qquad (15)$$

Thus zinc soap affects the rate for producing the effective radical MS· only by reacting with MSH, which is formed from MSSM by Reaction 4″. This mechanism of activation by zinc soap will be discussed again later.

Mechanism of formation of TBP from zinc soap.—The formation of the reaction product PS has been reported already in the previous papers as follows.

$$Ph_2CH^{\cdot} + {}^{\cdot}S_x{}^{\cdot} \longrightarrow Ph_2CHSx^{\cdot} \qquad (5)$$

$$2Ph_2CHS_x{}^{\cdot} \longrightarrow Ph_2CHS_{2x}CHPh_2 \qquad (7)$$

Table I indicates that the yield of TBP predominates over that of PS at the earlier stage of the reaction, that is, in the presence of a sufficient amount of the soap. Part VII of this series interpreted the predominance of TBP over PS by the following reaction between zinc soap and the radical $Ph_2CHS_x{}^{\cdot}$.

$$2Ph_2CHS_x{}^{\cdot} + (RCOO)_2Zn \longrightarrow 2Ph_2C{=}S + 2RCOOH + ZnS_{2x-2} \qquad (6')$$

The relation between (PS + TBP) and (ZnS + ZMBT + (MBT)/2), the data for which are given in Table I, is now discussed. In Part VII it was reported that the similar relationship (PS + TBP) = ZnS held among the products in the reaction involving DPM, sulfur, MBT and zinc butyrate, and in Part V the relationship (PS + TBP) = H_2S + (MBT)/2 held among the products in the reaction involving DPM, sulfur and MBTS. In the present study both TBP and PS are the dehydrogenated products from DPM, and MBT is the hydrogenated product from MBTS. As Reaction 4″ indicates, MSH corresponds to the radical $Ph_2CH^{\cdot}$, which leads to one half mole of PS as the Reactions 5 and 7 show. By considering the hydrogen balance, PS must be equivalent to 2MSH. However, 2MSH are converted to MSZnSM, forming 2 moles of fatty acid, which is a hydrogenated product from the soap. Therefore, from the point of view of hydrogen balance, one mole of ZMBT also corresponds to one mole of PS. Since ZMBT in turn decomposes to zinc sulfide, one mole of zinc sulfide corresponds to one mole of ZMBT and to one mole of PS as well. Reaction 6′ indicates that two of $Ph_2CHS_x{}^{\cdot}$ produce two moles of TBP and another mole of zinc sulfide. Formation of two moles of TBP from starting hydrocarbon DPM is accompanied by formation of two moles of zinc sulfide.

Therefore, the overall relationship among the products (PS + TBP) = (ZnS + ZMBT + MBT/2) holds from the point of view of hydrogen balance. This relation will be discussed again later.

Individual yields of products in this reaction vary as the reaction proceeds. Since the concentration of MBTS is sufficiently large at the earlier stage of the reaction, the amount of (ZMBT + MBT/2) predominates over ZnS, but when the concentration of MBTS decreases and of ZMBT increases, ZnS predominates over (ZMBT + MBT/2). While the concentration of zinc soap is sufficiently large, TBP in the left side of this relation predominates over PS. But as zinc soap is consumed during the reaction, PS predominates over TPB.

At a smaller concentration of the soap, hydrogen sulfide must evolve in place of zinc sulfide.

Formulation of the theoretical equations.—By applying the stationary state method, the rate equation for MBTS consumption will be derived from the elementary reaction steps mentioned above. At the stationary state the initial concentration of zinc butyrate is considered to be sufficiently large, and its consumption can be neglected. At this state only TBP is formed. All the necessary elementary reaction steps are again indicated below for the convenience of calculation.

$$\mathrm{MSSM} \xrightarrow{k_{10}} 2\mathrm{MS}\cdot \tag{10}$$

$$\mathrm{MS}. + \mathrm{S_8} \xrightarrow{k_{11}} \mathrm{MS}\cdot + \cdot\mathrm{S_x}\cdot \tag{11}$$

$$\mathrm{MSSM} + .\mathrm{S_x}. \xrightarrow{k_{13}} 2\mathrm{MS}\cdot + \cdot\mathrm{S_x}\cdot \tag{13}$$

$$\mathrm{MS}\cdot + \mathrm{Ph_2CH_2} \xrightarrow{k_4''} \mathrm{MSH} + \mathrm{Ph_2CH}. \tag{4''}$$

$$2\mathrm{MSH} + (\mathrm{RCOO})_2\mathrm{Zn} \xrightarrow{k_{17}} \mathrm{MSZnSM} + 2\mathrm{RCOOH} \tag{17}$$

$$\mathrm{MSZnSM} + \mathrm{S_8} \xrightarrow{k_{14}} 2\mathrm{MS}\cdot + \mathrm{ZnS_8} \tag{14}$$

$$\mathrm{MSZnSM} + \cdot\mathrm{S_x}\cdot \xrightarrow{k_{16}} 2\mathrm{MS}\cdot + \mathrm{ZnSx} \tag{16}$$

$$\mathrm{Ph_2CH}\cdot + \cdot\mathrm{S_x}\cdot \xrightarrow{k_5} \mathrm{Ph_2CHS_x}\cdot \tag{5}$$

$$2\mathrm{Ph_2CHS_x}. + (\mathrm{RCOO})_2\mathrm{Zn} \xrightarrow{k_6'} 2\mathrm{Ph_2C{=}S} + 2\mathrm{RCOOH} + \mathrm{ZnS_{2x-2}} \tag{6'}$$

$$\mathrm{ZnS_x} \xrightarrow{k_{15}} \mathrm{ZnS} + \cdot\mathrm{S_{x-1}}\cdot \tag{15}$$

Applying the stationary state method, the following relations are obtained.

$$\mathrm{d}[\cdot\mathrm{S_x}\cdot]/\mathrm{d}t = k_{11}[\mathrm{MS}\cdot][\mathrm{S_8}] - k_{16}[\mathrm{MSZnSM}][\cdot\mathrm{S_x}\cdot] - k_5[\mathrm{Ph_2CH}.][\cdot\mathrm{S_x}\cdot] + k_{15}[\mathrm{ZnS_x}] = 0 \tag{i}$$

$$\mathrm{d}[\mathrm{MS}\cdot]/\mathrm{d}t = 2k_{10}[\mathrm{MSSM}] + 2k_{13}[\mathrm{MSSM}][\cdot\mathrm{S_x}\cdot] - k_4''[\mathrm{MS}\cdot][\mathrm{Ph_2CH_2}] + 2k_{14}[\mathrm{MSZnSM}][\mathrm{S_8}] + 2k_{16}[\mathrm{MSZnSM}][\cdot\mathrm{S_x}\cdot] = 0 \tag{ii}$$

$$\mathrm{d}[\mathrm{Ph_2CH}\cdot]/\mathrm{d}t = k_4''[\mathrm{MS}\cdot][\mathrm{Ph_2CH_2}] - k_5[\mathrm{Ph_2CH}\cdot][\cdot\mathrm{S_x}\cdot] = 0 \tag{iii}$$

$$\mathrm{d}[\mathrm{Ph_2CHS_x}\cdot]/\mathrm{d}t = k_5[\mathrm{Ph_2CH}\cdot][\cdot\mathrm{S_x}\cdot] - 2k_6'[\mathrm{Ph_2CHS_x}\cdot][(\mathrm{RCOO})_2\mathrm{Zn}] = 0 \tag{iv}$$

$$\mathrm{d}[\mathrm{ZnS_x}]/\mathrm{d}t = k_{14}[\mathrm{MSZnSM}][\mathrm{S_8}] + k_{16}[\mathrm{MSZnSM}][\cdot\mathrm{S_x}\cdot] + k_6'[\mathrm{Ph_2CHS_x}\cdot][(\mathrm{RCOO})_2\mathrm{Zn}] - k_{15}[\mathrm{ZnS_x}] = 0 \tag{v}$$

From (iii) and (iv),

$$2k_6'[Ph_2CHS_x\cdot][(RCOO)_2Zn] = k_5[Ph_2CH][\cdot S_x\cdot] = k_4''[MS\cdot][Ph_2CH_2] \quad \text{(vi)}$$

Putting (vi) in a relation obtained by adding (i) to (v),

$$k_{11}[MS\cdot][S_8] + k_{14}[MSZnSM][S_8] - (\tfrac{1}{2})k_4''[MS\cdot][Ph_2CH_2] = 0 \quad \text{(vii)}$$

From (ii) and (vii),

$$[\cdot S_x\cdot] = \frac{k_{11}[MS\cdot][S_8] - k_{10}[MSSM]}{k_{13}[MSSM] + k_{16}[MSZnSM]} \quad \text{(viii)}$$

The rate equation for MSSM consumption is derived from the elementary steps as follows.

$$-\,d[MSSM]/dt = k_{10}[MSSM] + k_{13}[MSSM][\cdot S_x\cdot] \quad \text{(ix)}$$

Putting (viii) in (ix),

$$-\,d[MSSM]/dt = \frac{k_{10}k_{16}[MSZnSM] + k_{11}k_{13}[MS\cdot][S_8]}{k_{13}[MSSM] + k_{16}[MSZnSM]}\cdot[MSSM] \quad \text{(x)}$$

In order to integrate (x), a relation between [MSSM] and [MSZnSM] is necessary.
Since MSSM is converted to MSZnSM and MSH,

$$[MSSM]_0 - [MSSM] = [MSZnSM] + [MSH]/2, \quad \text{(xi)}$$

where $[MSSM]_0$ represents initial concentration of MSSM. Putting (xi) in (x),

$$-\,d[MSSM]/dt = \frac{[MSSM]_0 - [MSSM] - [MSH]/2 + (k_{11}k_{13}/k_{10}k_{16})[MS\cdot][S_8]}{[MSSM]_0 - [MSH]/2 - (1 - k_{13}/k_{16})[MSSM]} \times k_{10}[MSSM] \quad \text{(xii)}$$

For the sake of brevity, $k_{11}[MS\cdot][S_8]$ is replaced by a constant e. At the stationary state, [MS.] is constant, and at the earlier stage of the reaction $[S_8]$ is considered to be constant, since $[S_8]$ is sufficiently large as compared with sulfur consumption. Thus e is constant. Then,

$$(k_{11}k_{13}/k_{10}k_{16})[MS\cdot][S_8] = e' = (k_{13}/k_{10}/k_{16})e$$

In the presence of sufficient amount of zinc soap, that is, at the stationary state, MSH is converted to MSZnSM immediately after the former is formed from MSSM. Therefore, [MSH] can be neglected as compared with [MSSM]. By considering the above relation and putting e', relation (xii) reduces to (xiii),

$$-\frac{[MSSM]_0 - (1 - k_{13}/k_{16})[MSSM]d[MSSM]}{\{[MSSM]_0 + e' - [MSSM]\}[MSSM]} = k_{10}dt \quad \text{(xiii)}$$

Equation (xiii) has a quite similar type to the equation obtained in Part V on the reaction involving DPM, sulfur and MBTS. Integrating (xiii) and considering that a relation

$$\frac{[\mathrm{MSSM}]_0 + e' - [\mathrm{MSSM}]}{e'} = 1$$

holds at the initial stage of the reaction,

$$\log \frac{[\mathrm{MSSM}]_0}{[\mathrm{MSSM}]} = \frac{[\mathrm{MSSM}]_0 + e'}{[\mathrm{MSSM}]_0} \cdot k_{10} t \qquad (\mathrm{A})$$

Equation (A) will be proved experimentally later.

The relation (PS + TBP) = (ZnS + ZMBT + (MBT)/2) cited before can be derived from elementary steps as follows. As the definition of the stationary state indicates, not PS but only TBP is formed at this stage.

$$\mathrm{d}[\mathrm{Ph_2C{=}S}]/\mathrm{d}t = 2k_6'[\mathrm{Ph_2CHS_x}\cdot][(\mathrm{RCOO})_2\mathrm{Zn}] = k_4''[\mathrm{MS}\cdot][\mathrm{Ph_2CH_2}]$$

And by using (v),

$$\mathrm{d}[\mathrm{ZnS}]/\mathrm{d}t + \mathrm{d}[\mathrm{MSZnSM}]/\mathrm{d}t + (\mathrm{d}[\mathrm{MSH}]/\mathrm{d}t)/2 = k_4''[\mathrm{MS}\cdot][\mathrm{Ph_2CH_2}]$$

By comparing the above two relations,

$$\mathrm{d}[\mathrm{Ph_2C{=}S}]/\mathrm{d}t = \mathrm{d}[\mathrm{ZnS}]/\mathrm{d}t + \mathrm{d}[\mathrm{MSZnSM}]/\mathrm{d}t + (\mathrm{d}[\mathrm{MSH}]/\mathrm{d}t)/2 \qquad (\mathrm{B})$$

The Equation (B) will represent accelerating efficiency of MBTS, and will be discussed again later.

Comparison of the theoretical equations with experimental results.—The theoretical Equation (A) will be examined experimentally. Table II shows the relation between the reaction conditions and experiment numbers. This relationship is applied to all the experiments carried out through the present paper. Figure 1A indicates the relation between reaction time and log ($[\mathrm{MSSM}]_0/[\mathrm{MSSM}]$), e.g., rates for MBTS consumption at 160° C for various experiments. The same relation at 140 and 150° is shown in Figure 1B. In drawing Figure 1A and 1B, [MSSM] can be obtained by determining [MSZnSM] and [MSH], and by putting these values in the relation (xi). Since Experiment 2 in Figure 1A has a higher $[\mathrm{MSSM}]_0$ value than the other, it consumes zinc soap faster. Therefore, the stationary state represented by the straight

TABLE II

EXPERIMENT NUMBERS AND THEIR REACTION CONDITIONS

Experiment No.	Temp., °C	Reaction conditions		
		$[(\mathrm{RCOO})_2\mathrm{Zn}]_0$	$[\mathrm{MSSM}]_0$ (mole·l^{-1})	$[\mathrm{S_8}]_0$
1	160	0.5	0.1	0.1
1′	150	0.5	0.1	0.1
1″	140	0.5	0.1	0.1
2	160	0.5	0.2	0.1
3	160	0.25	0.05	0.1
4	160	0.5	0.05	0.1

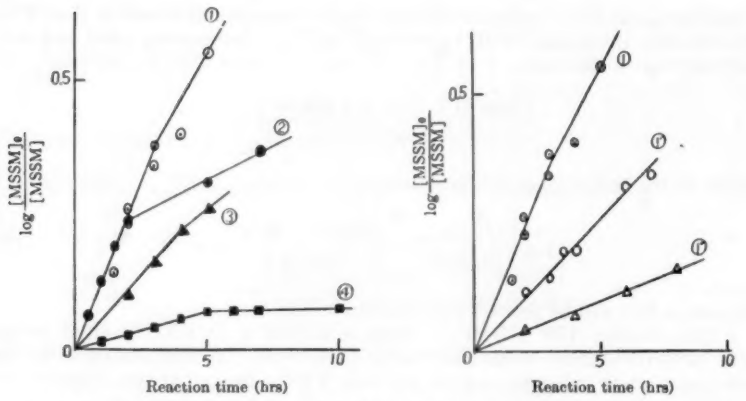

FIG. 1A and 1B.—Rates for MBTS consumption. As to experiment numbers and the reaction conditions, see Table II. 1A is the left and 1B the right hand figure.

line in Figure 1 persists for shorter period in No. 2 than in the other. On the other hand, Figure 1B indicates that the stationary state of the reaction at lower temperatures persists for a longer time because of the slower consumption for zinc soap. In any case, at the earlier stage of the reaction, where [MSSM] = $[MSSM]_0$ holds, Equation (A) is proved experimentally as far as the straight lines exist. The same linear relationship between $\log [MSSM]_0/[MSSM]$ and reaction times was already reported in the reaction involving DPM, sulfur and MBTS in the absence of zinc soap.

The slopes of straight lines in Figure 1 must represent $k_{10}([MSSM]_0 + e')/[MSSM]_0$ as shown in Equation A. These values of Experiments 1, 1′, and 1″ were obtained from Figure 1B and plotted against $1/T$ in Figure 2. In Part V of this series, which reported the reaction involving DPM, sulfur and MBTS in

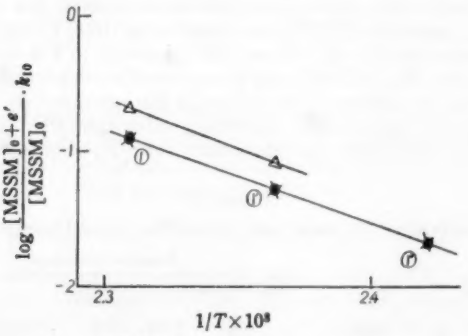

FIG. 2.—Relation between $\log\left(\frac{[MSSM]_0+6'}{[MSSM]_0}\cdot k_{10}\right)$ and $1/T$. —×—×— represents the results of the present paper and —△—△— —●—●— represent the results of Part V, i.e., the relation between $\log\left(\frac{[MSSM]_0\, e'}{[MSSM]_0}\, k_{10}\right)$ and $1/T$.

the absence of zinc soap, the values of log (k_{10}([MSSM]$_0$ + $c'/2$)[MSSM]$_0$) were also plotted against $1/T$, where c' represents a constant similar to e' in the present paper. This result is also shown in Figure 2. Two lines of Part V are parallel to a line obtained in the present paper. Complete overlapping of one of those lines with the latter may have no significance. Distance parallel to the ordinate between the lines represents the difference in the values between log ([MSSM]$_0$ + e')/[MSSM]$_0$ and log ([MSSM]$_0$ + $c'/2$)/[MSSM]$_0$. The apparent activation energy of the thermal dissociation of MBTS, can be obtained from Figure 2. This was found to be 32.7 kcal/mole. Quite the same value, of course, was found in Part V.

The theoretical Equation (B) will be examined next. The values of {[ZnS] + [MSZnSM] + [MSH]/2}, which represent accelerating efficiency of MBTS as stated in the preceding sections, are plotted against reaction time in Figure 3. Straight lines which appear at the earlier stage of the reaction in

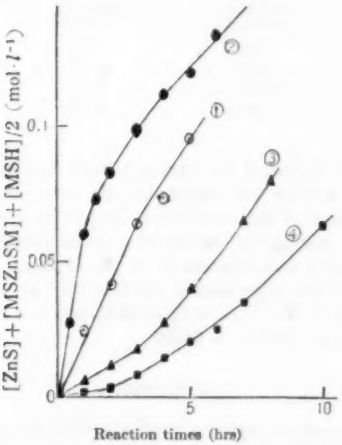

FIG. 3.—Accelerating Efficiency of MBTS. As to the experiment numbers, see Table II.

Figure 3 as in Figure 1 indicate experimental proof for Equation (B). The reason why some curves in Figure 3A are concave and the others are convex to the ordinate is as follows. In Experiments 3 and 4, the accelerating efficiency increases as the reaction proceeds. In these experiments the initial concentration of MBTS is lower and therefore, the consumption of zinc soap is slower than in the other. Then it leads to a rection with sulfur and MBT in the presence of zinc soap. On the other hand, in Experiments 1 and 2 the initial concentration of MBTS is higher and the consumption of zinc soap is faster than in Experiments 3 and 4. Then it leads to a reaction with sulfur and MBT in the absence of the soap. It can be said that the reaction with sulfur and MBTS in the presence of the soap is shifting gradually to the reaction with sulfur and MBT either in the presence or in the absence of zinc soap, depending on the initial concentration of MBTS. Since the accelerating efficiency of MBT in the absence of zinc soap is lower than that of MBTS in the presence of the soap, if both are in the same accelerating concentrations, the curvature

for the plots for Experiments 1 and 2 decreases with time. On the other hand, since the efficiency of MBT is considered to be higher than that of MBTS both in the presence of the soap, the curves for Experiments 3 and 4 are steeper at longer times.

From Equation (B) the slope of the straight lines represent the values of $k_4''[MS\cdot][Ph_2CH_2]$, which is modified to $e(k_4''/k_{11})[Ph_2CH_2]/[S_8]$ by applying the relation $e = k_{11}[MS\cdot](S_8]$. Putting $[Ph_2CH_2]_0$ and $[S_8]_0$ in place of $[Ph_2CH_2]$ and $[S_8]$, respectively, the values of $e(k_4''/k_{11})$ can be calculated from the slopes of the straight lines in Figure 3A. These values are shown in Table III. As stated above the value of $k_{10}([MSSM]_0 + e')/[MSSM]_0$ can

TABLE III

THE VALUES OF e AND e' CALCULATED FROM THE EXPERIMENTAL DATA

No.	$(k_4''/k_{11})e$ observed	e' calculated when k_{10} =0.006	$e'/(k_4''/k_{11})e$
1	1.387	1.90	1.37
2	3.072	4.13	1.34
3	0.344	0.45	1.31
4	0.162	0.21	1.30

be obtained from the slopes of the straight lines in Figure 1A. Although the real value of k_{10} can not be calculated by any method, the value of e' can be evaluated by the method of trial and error, that is, by assigning arbitrary values to k_{10}. When $k_{10} = 0.006$, the values of e' thus calculated are also listed in Table III. Considering the relation $e' = (k_{13}/k_{10}k_{16})$, the value of e'/e must be a constant for every experiment carried out at the same temperature. Table III shows that $e'/(k_4''/k_{11})\cdot e$ thus obtained is a constant, and a nearest approach value of k_{10} at 160° C is 0.006.

SYNOPSIS

The reaction products of diphenylmethane (DPM) with sulfur and 2-benzothiazolyl disulfide (MBTS) in the presence of zinc butyrate were benzhydryl polysulfides, thiobenzophenone (TBP), zinc salt of 2-mercaptobenzothiazole (ZMBT) and ZnS. They were quite the same as those of the reaction involving DPM, sulfur, zinc butyrate and 2-mercaptobenzothiazole (MBT). It was concluded from this result that the mercaptobenzothiazolyl radical, which is generated by homolytic dissociation of MBTS, dehydrogenates DPM and is converted to MBT. As reported in the previous paper, the latter compound interacts with zinc butyrate to form ZMBT which in the presence of sulfur generates the 2-mercaptobenzothiazolyl radical. This radical takes part in the accelerating mechanism by splitting the sulfur ring molecule. When a sufficient amount of zinc butyrate was present in the reaction system, only TBP was formed by the action of zinc butyrate, and a relationship (TBP in moles = ZnS + ZMBT + $(\frac{1}{2})$MBT in moles) held. Then a stationary state existed, at which rate equations for MBTS consumption and for TBP formation could be derived theoretically from the reaction mechanism. The theoretical equations were found to fit experimental results. The effect of zinc butyrate on MBTS acceleration was thus deduced to be as follows: only when it interacts with MBT, which is formed from MBTS to produce ZMBT, does it affect the

rate of sulfuration (vulcanization). The lesser efficiency of either zinc soap or zinc oxide with fatty acid on MBTS acceleration than on MBT acceleration, which is well-known for rubber technologists, may be interpreted by the mechanism cited.

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[1] Tsurugi, J. and Nakabayashi, T., RUBBER CHEM. & TECHNOL. **31**, 779 (1958).
[2] Tsurugi, J. and Fukuda, H., RUBBER CHEM. & TECHNOL. **31**, 788 (1958).
[3] Tsurugi, J. and Fukuda, H., RUBBER CHEM. & TECHNOL. **33**, 211 (1960).
[4] Tsurugi, J., RUBBER CHEM. & TECHNOL. **31**, 762 (1958).
[5] Tsurugi, J., and Fukuda, H., RUBBER CHEM. & TECHNOL. **33**, 217 (1960).
[6] As mentioned previously the true accelerator is the 2-mercaptobenzothiazolyl radical. Since MBT can supply one and MBTS has two of these, one half mole of MBTS is equivalent to one mole of MBT with regard to accelerating efficiency.

THE VULCANIZATION OF NEOPRENE WITH N,N′-DINITROSO-*p*-PHENYLENE-BIS(HYDROXYLAMINE) SALTS, A NEW CLASS OF CURING AGENTS

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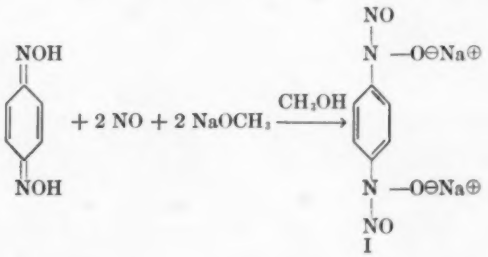
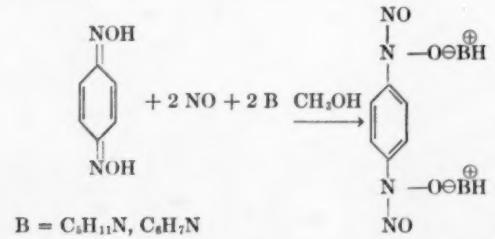
The reaction of nitric oxide with *p*-benzoquinonedioxime in the presence of sodium methoxide to form disodio-N,N′-dinitroso-*p*-phenylene-bis (hydroxylamine) (I) in 96% yield has recently been reported[1]. When a water solution of I is treated with soluble metallic salts of Zn^{++}, Ca^{++}, Mg^{++}, etc., the corresponding N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) salt is obtained. Stable organic salts can be isolated when the bases piperidine or aniline are employed in place of sodium methoxide. Adducts have also been obtained



I

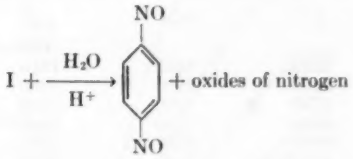
using piperazine and ethylenethiourea, but the structures of these materials have not been clarified.



B = $C_5H_{11}N$, C_5H_7N

During a study of structure, it was found that I, under the influence of an acidic environment decomposed to form *p*-dinitrosobenzene (70%), a small quantity of an unidentified material, and oxides of nitrogen. Besides showing that the ring carbon atoms were not attacked, this brought to light the prospect that these materials could act as vulcanizing agents. The reactivity of olefinic

linkages with nitroso groups and the relationship of these transformations to crosslinking activity have been investigated to some extent[2,3,4,5].



By analogy with the Bruni-Geiger reactions in natural rubber[6], the investigations of Pummerer and Gündel[7], and the proposal of Flory and Rehner for the vulcanization of butyl[8], liberation of *p*-dinitrosobenzene from the bis-(hydroxylamine) under the acidic conditions encountered in neoprene (Equa-

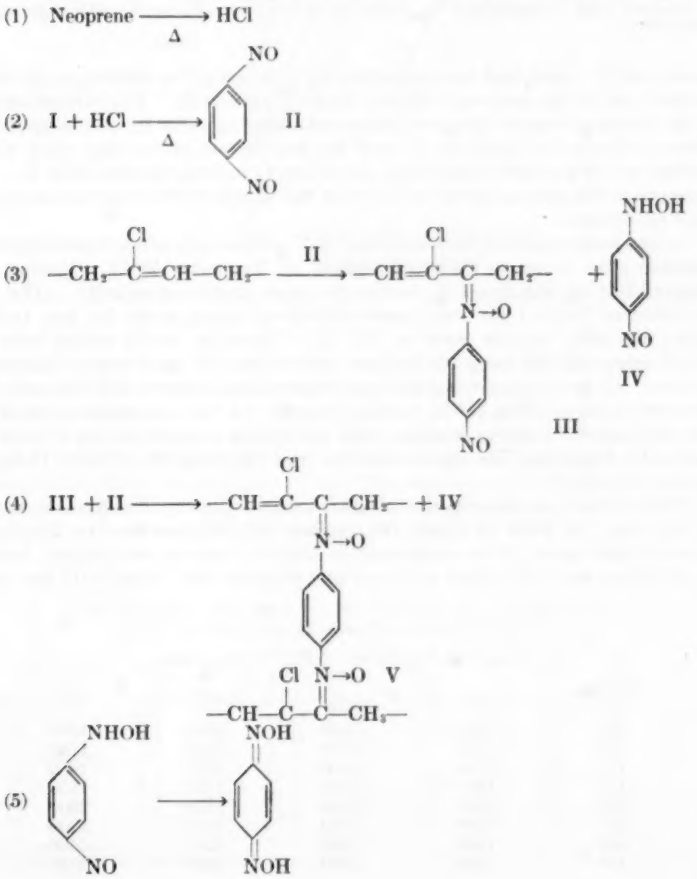


TABLE I [a]

ULTIMATE TENSILE [b], T_B FOR NEOPRENE WRT [c, d] CURED AT 307° F WITH THE ZINC SALT OF N,N′-DINITROSO-*p*-PHENYLENE-BIS(HYDROXYLAMINE)

Parts	T_B^{10}	T_B^{20}	T_B^{30}	T_B^{60}
0.0			630	800
0.5	1570	1910	1910	1970
0.75	1430	1920	2060	2260
1.0	1740	1780	2230	2310
1.5	1750	2240	2360	2210
2.0	1590	2060	2150	2240
2.5	1850	2345	2510	2520
3.0	1770	2540	2430	2512
4.0	1980	2610	2420	2440

[a] Five values were obtained for each cure and the average of the four closest was used to compute the values given.

[b] T_B = tensile at break. The number following T_B signifies minutes of cure.

[c] Formulation for these data included Neoprene WRT (100), Micronex W-6 (40). These amounts of rubber and carbon black were employed for all recipes unless otherwise noted.

[d] Neoprene WRT containing no sulfur, thiuram disulfide or other components capable of decomposing to give sulfur.

tions 1 and 2), could lead to crosslinking by reaction of the nitroso group with a double bond in the neoprene rubber chain (Equation 3). The bifunctionality of the dinitrosobenzene then enables crosslinking to occur by a subsequent reaction analogous to Equation 3, since the free nitroso group may react with a double bond of a neighboring chain (Equation 4) to form the dinitrone V. The structure of the nitroso group is shown in the simplest conventional manner in these equations.

As had been expected, various salts of N,N′-dinitroso-*p*-phenylenebis(hydroxylamine) were found to be curing agents in Neoprene WRT. During preliminary testing, the zinc salt showed the most promising activity. The data are listed in Table I for varying quantities of curing agent for ten, twenty, thirty, and sixty minute cures at 307° F. Optimum tensile values were obtained using 3.0–4.0 parts of the zinc salt for twenty and thirty minute exposures. Controls employing the base formulation without the zinc salt were heat cured only. The 300% modulus values for the vulcanizates show the rate and state of cure to increase with increasing concentrations of zinc salt (Table II, Figure 1). The superscript numbers following M in Table II signify minutes of cure.

Table III shows the results obtained using a variety of salts. It was expected that the salts of piperazine, aniline and ethylenethiourea would give superior cures since, if the amine and *p*-dinitrosobenzene are initially formed, N-alkylation can take place at the active chlorine site[9], along with the action

TABLE II

M_{300} FOR NEOPRENE WRT VULCANIZATES

(Zinc salt) parts	M_{300}^{10}	M_{300}^{20}	M_{300}^{30}	M_{300}^{60}
0.5	950	1100	1200	1500
0.75	975	1100	1300	1700
1.0	1100	1300	1650	1850
1.5	1100	1350	1700	1950
2.0	1100	1550	1550	2000
2.5	1200	1700	1950	2200
3.0	1300	1850	2250	2400
4.0	1450	2200	2500	2480

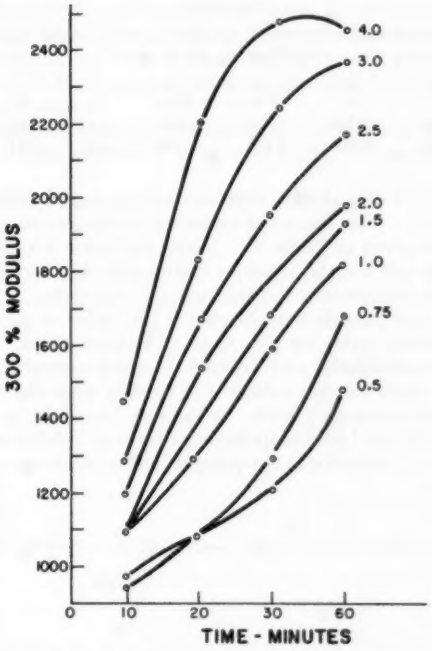


FIG. 1.—Effect of concentration of zinc salt on state and rate of cure. The numbers on each curve indicate phr or zinc salt.

of the nitroso groups. This, however, was not the case. Comparison of the sodium and lithium salts also showed a surprising difference.

The temperatures at which the maximum curing rate took place were obtained for each of three materials by differential thermal analysis and were Na^{+} 390° F, Zn^{++} 348° F, and Mg^{++} 398° F. After a specimen of neoprene containing 2.5 phr of the zinc salt (Table IV) was exposed to 307° F for twenty minutes, curing had virtually ceased, while the corresponding Na^{+} and Mg^{++} stocks still showed considerable activity at 390 and 398° F, respectively.

TABLE III

VULCANIZATION ACTIVITY OF N-N′-DINITROSO-*p*-PHENYLENE-BIS(HYDROXYLAMINE) IN NEOPRENE WRT

Salt	Parts	T_B^{20}	T_B^{30}	M_{300}^{20}	M_{300}^{30}	E^{20}	E^{30}	S^{20}	S^{30}
Piperazine	2.5	1560	2040	1150	1400	450	430	5	5
Piperidine	2.5	1330	1480	900	950	500	480	9	8
Aniline	2.5	1780	1800	1300	1350	400	400	4	4
Ethylenethiourea	2.5	1980	2130	—	—	280	280	3	2.5
Mg^{++}	2.5	1310	1720	700	800	570	520	12	9
Ca^{++}	2.5	1500	2100	850	1150	500	470	7.5	6
Li^{+}	2.5	1540	1950	900	1050	500	500	8	7

E = elongation at break, %.
S = permanent set after breaking, %.

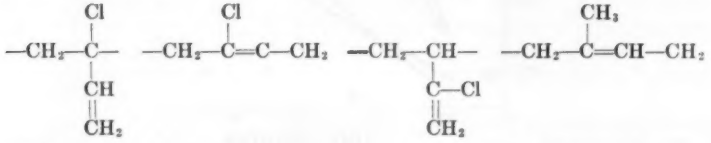
TABLE IV

COMPARATIVE ACTIVITY OF ZINC AND SODIUM SALTS (2.5 PARTS) AT 307° F

Salt	T_B^{20}	T_B^{30}	M_{300}^{20}	M_{300}^{30}	E^{20}	E^{30}	S^{20}	S^{30}
Zn^{++}	2345	2510	1700	1950	400	375	5	4
Na^{+}	2170	2420	1300	1700	450	390	5	4

Samples of the latter two stocks were completely cured after twenty minute exposure at 350° F. The optimum cures for comparative vulcanizates with these materials are given in Table V. Under optimum conditions for all compounds the sodium salt showed superior curing activity. Appropriate controls were considered in interpreting the thermal analysis data.

A few further experiments were carried out in order to gain some idea as to a possible mechanistic path for this type of vulcanization. The mechanism defined above was anticipated and, thereby, it was assumed that no interaction would take place when natural rubber was treated with the N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) salts. This was found to be the case. The polymerization units for both neoprene and natural rubber are shown below. The allylic chorine of neoprene is not present in the backbone of natural rubber.



1,2 Neoprene 1,4 3,4 Natural

Obviously, then, with natural rubber there is no source of hydrochloric acid and no reactive site for SN_2' displacement. The 1,4 and 3,4 polymerization units present in the neoprene polymer contain only inactive vinylic chloride. No interaction took place when natural rubber containing the sodium salt of N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) was exposed to temperatures above 500° F. The importance of the allylic chlorine in neoprene is accordingly believed to be great.

A sample of neoprene WRT in benzene was then treated with piperidine at reflux temperature for fourteen hours. The allylic chloride was thereby removed from the polymer, and after reprecipitation and air drying, 2.5 parts of the sodium salt and 40 parts of carbon black (Micronex W-6) were milled with 100 parts of the amine-treated neoprene. Differential thermal analysis indicated a cure rate peak at 530° F. The possibility of a *p*-dinitrosobenzene cure

TABLE V[a]

MAXIMUM VULCANIZING ACTIVITY IN NEOPRENE WRT

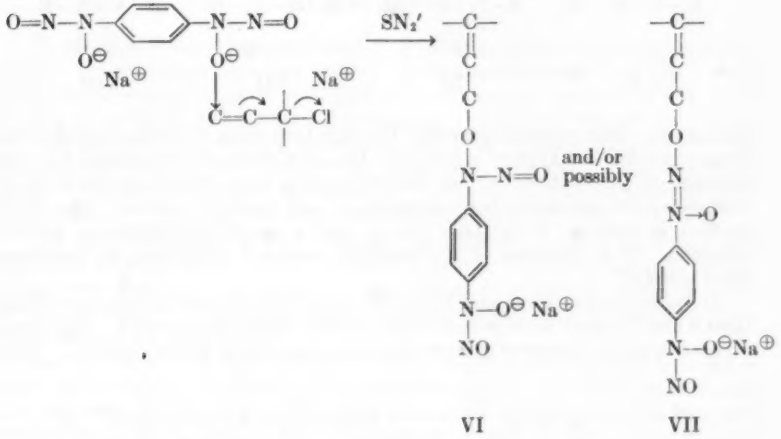
Salt	Max. Cure Temperature, ° F	Cure Temperature, ° F	T_B	E	S
Na^{+}	390	330	2750	330	2
Zn^{++}	348	307	2345	400	5
Mg^{++}	398	350	2300	400	4

[a] The physical properties listed are for twenty minute cures at temperatures shown.

was thus considerably diminished and the more likely path thus may involve an SN_2' attack at the allylic chloride. Primarily the anion would attack as shown in Equation 6, and the bifunctionality would permit crosslinking to occur by virtue of the same type of reaction (Equation 7) with an allylic position in another polymer chain.

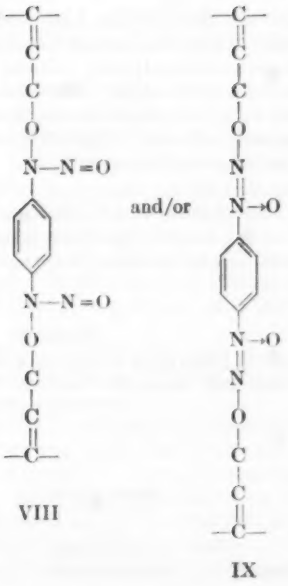
Primarily for simplification, the crosslinks VIII and/or IX are shown as the β form and one of the possible α form structures. These type materials have

(6)



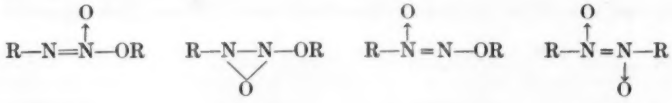
VI VII

(7) VI (VII) + C=C—C(Cl)—Cl ⟶



VIII IX

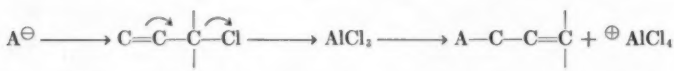
been made using the silver salt of nitrosohydroxylamines[10,11]. The structure of the α form has not been proved. Hantzsh[12] has suggested structure X, while Bamberger and Ekecrantz[13] suggested either XI ro XII. More recently, structure XIII has been added to the list of possibilities[14] although it is in conflict with one structure proposed for nitroso dimers[15,16,17,18,19]. The cross-



X XI XII XIII

linking may take place in neoprene through formation of both α and β forms. Precedence for this type of reaction in this new series of compounds has been obtained in the synthesis of the dimethyl ether from the silver salt of N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) and methyl iodide. The latter product is believed to be the α isomer since a negative Liebermann test was obtained. The structure of the reacting species I must also be considered more closely[20].

If vulcanization involves SN_2' attack at the active site in neoprene (Equations 6 and 7) catalytic effects of heavy metals might be expected. One would expect the acidic nature of these to facilitate removal of active chloride. When



aluminum or zinc are added to the base formulation of the disodium salt, this effect is observed. Also, when amine treated neoprene was used with zinc, the curing temperature was considerably reduced (Table VI). Differential thermal analysis indicated a possible initial formation of metal halide in simple neoprene recipes, followed by a decreased maximum cure rate temperature when compared to the uncatalyzed case. Table VII shows the comparison of the physical properties for these vulcanizates.

The data clearly indicate that a higher rate and state of cure are attained when stoichiometric quantities of aluminum powder are incorporated in the recipe. When excess metal or too long a curing time (30 minutes at 307° F) is employed, side or clevage reactions take place resulting in lower quality vulcanizates.

TABLE VI

CATALYTIC EFFECTS OF METALS ON VULCANIZATION OF NEOPRENE AND AMINE-TREATED NEOPRENE USING THE DISODIUM SALT OF N,N′-DINITROSO-*p*-PHENYLENE-BIS-(HYDROXYLAMINE)

		Maximum cure rate (° F)				
		Neoprene			Aminated neoprene	
Material	Decomposition point (° F)	—	Zn	Al	—	Zn
Na^+ Salt	632	390	324	308	530	410
Neoprene WRT	begins > 580		—		—	
Amine-treated neoprene	begins > 600		—		—	

TABLE VII

VULCANIZATION OF NEOPRENE WRT AT 307° F (20 MIN.) WITH DISODIO N,N′-DINITROSO-*p*-PHENYLENE-BIS(HYDROXYLAMINE) (2.5 PHR)

Catalyst (parts)	T_S	M_{300}	S	E
—	2170	1300	5	450
0.5 Aluminum	2600	1700	4	400

EXPERIMENTAL

Preparation of the disodium salt of N,N′-dinitroso-p-phenylene-bis(hydroxylamine). Magne-Dash autoclave method.—*p*-Benzoquinonedioxime (70 g, 0.51 mole) was dissolved in methanol (500 ml.) and sodium methoxide (54 g, 1.0 mole) was added to the solution with stirring. The resulting brown mixture was placed in a Magne-Dash autoclave, and after flushing thoroughly with nitrogen, the system was charged with nitric oxide (100 psi). The take up of nitric oxide was quite rapid, necessitating a recharge of the autoclave at various intervals. Reaction was completed within fifteen minutes.

The dark brown reaction mixture was then filtered, washed with methanol and after drying 110 g (91%) of N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) was obtained. Although reaction is somewhat slower, excellent yields (90%) are afforded by use of an aqueous sodium hydroxide medium rather than methanol-sodium methoxide.

Low pressure Paar hydrogenator method.—Aniline (18.9 g, 0.2 mole) was added to a solution of *p*-benzoquinonedioxime (13.8 g, 0.1 mole) in methanol (100 ml) and after flushing with dry nitrogen, nitric oxide was admitted and pressurized to 60 psi, using a Paar hydrogenator equipped with a stainless steel tank and pressure gage. Recharging and shaking was continued until no further absorption of gas was apparent. After filtration and drying of the brown precipitate, 25 g (66%) of di-anilino-N,N′-dinitroso-*p*-phenylene-bis-(hydroxylamine) was obtained.

All salts may be prepared on small scale using this method. Ethylenethiourea (10.2 g, 0.1 mole) and *p*-benzoquinonedioxime (13.8 g, 0.1 mole) gave 60% product; and using piperazine, di-piperazino-N,N′-dinitroso-*p*-phenylene-bis-(hydroxylamine) was obtained. The lithium salt was prepared (77%) empolying aqueous lithium hydroxide.

Preparation of divalent cationic salts of N,N′-dinitroso-p-phenylene-bis-(hydroxylamine).—An aqueous solution of the zinc acetate (0.1 mole) was added dropwise to a water solution of the disodium salt (0.1 mole) with stirring. The zinc salt of N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine) precipitated and after filtration, washing with water and drying 16 g (69%) of the pure product was afforded.

The calcium (95%) and magnesium (88%) salts were also produced in this manner, using calcium chloride (dihydrate) and magnesium sulfate (heptahydrate) respectively.

Decomposition of disodium salt of N,N′-dinitroso-p-phenylene-bis(hydroxylamine).—The disodium salt (1.2 g) was added to 5 ml concentrated hydrochloric acid and warmed gently. Oxides of nitrogen were apparent (brown gas) above the aqueous mixture. After filtration and drying 0.5 g (73%) of a yellow solid was obtained. The infrared spectrum of the yellow solid was identical with that of an authentic sample of *p*-dinitrosobenzene.

The filtrate was neutralized and an unidentified yellow solid (0.16 g) was

collected and dried. The infrared spectrum of this material was similar to that of *p*-dinitrosobenzene, however, the strong band at 1245 cm^{-1} was lacking.

Preparation of amine-treated neoprene.—Neoprene WRT (100 g) was dissolved in benzene (1500 ml) and piperidine (250 g) was added. After the solution had been refluxed for fourteen hours, the organic layer was extracted with 1500 g of water. The benzene layer was dried over sodium sulfate, filtered and precipitated by slow addition to methanol. After three reprecipitations, the amine-treated neoprene was dried at 150° F for two hours before compounding.

An aliquot (100 g) of the aqueous extract was added to methanol (100 ml) and the solution was titrated with 0.1 *N* $AgNO_3$ solution conductimetrically. A Leeds-Northrup conductivity cell was used (const. −0.1) in conjunction with Industrial Instruments, Inc. conductivity bridge Model RD-1B. The

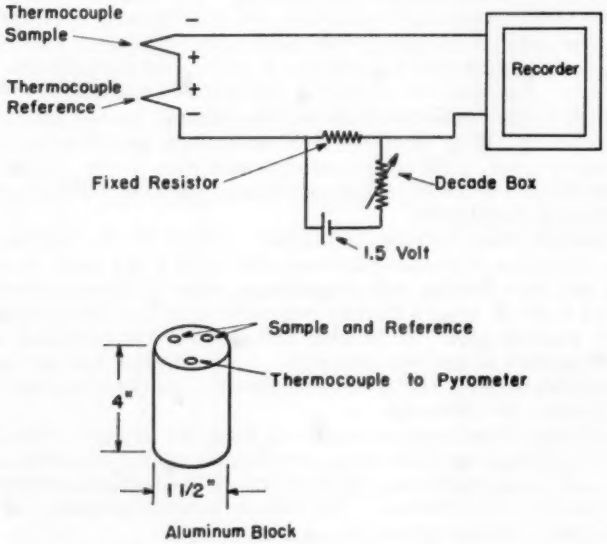


FIG. 2

titration reached an end point after addition of 10 ml of $AgNO_3$ solution (1.2% allylic chloride).

Thermal analysis.—The scheme shown in Figure 2 illustrates the apparatus employed to obtain thermal analysis curves. Using two thermocouples, one opposing the other in sample and reference cells, any difference in EMF is indicative of a change in heat in the sample. The thermocouples were inserted in small test tubes which were placed in a solid 4″ × 1½″ aluminum block. The block was then set in an electric furnace. A 1½ volt battery (Eveready No. 6) was used to oppose the EMF in order to maintain the recorder pen on scale on 1 mv full deflection (Barber-Colemen Co. MODEL 8000-600-8266). A decade box (0-100,000 OHMS) was employed for adjusting the base line at occurrence of endothermic and/or exothermic peaks.

With solid samples, 0.1 g of the solid material was mixed with 1 g of sand and 1 g of sand was used as the reference. The thermocouples, after insertion

into the samples, were glass taped to the top of the test tubes. A small hole drilled in the aluminum block held a third thermocouple which was connected to a pyrometer to record temperature. After insertion of this unit into the electric furnace, heating was applied and exothermic or endothermic interactions recorded.

With neoprene, butyl and natural rubbers, the rubber was milled to about $\frac{1}{16}''$ thickness and cut into $\frac{1}{2}''$ strips. These strips were wrapped tightly around the thermocouples. The same type of rubber, without additives, was used as a reference.

SYNOPSIS

A new series of materials, metallic and organic base salts of N,N′-dinitroso-*p*-phenylene-bis(hydroxylamine), have been shown to possess considerable vulcanizing activity in neoprene stocks. The path of the corsslinking reaction is discussed and evidence which is indicative of bisalkylation (α and/or β) of the allylic position is presented. Although no interaction occurs in natural rubber, amine-treated neoprene is also vulcanized with these materials. The vulcanization is catalyzed by aluminum and zinc, quite possibly via the metal halides formed in situ in Neoprene WRT.

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FIRST AND SECOND ORDER TRANSITIONS IN NEOPRENE *

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The proneness of neoprene to undergo first order transition, or crystallization, accounts for the rapid development of high bond strength by neoprene adhesives as well as for the high tensile strength of lightly loaded, unreinforced neoprene vulcanizates. In its capacity to crystallize, this synthetic elastomer is similar to natural rubber and unlike most synthetic elastomers which as a rule do not crystallize readily. Like all elastomers, noeprene stiffens when cooled and when its temperature is reduced sufficiently, undergoes the second order or glass transition. Common use of the terms "first order and second order transition" in the rubber industry to denote change to crystalline and glasslike conditions, respectively, is subject to question. Although used throughout this paper, it is recognized that first order transition in elastomers while approached is not actually fully achieved[4]. Likewise, the change to a glasslike condition is not strictly speaking a phase[5] change as might be implied by the term "second order transition".

Any pronounced stiffening which develops as a result of either first or second order transition may interfere with the low temperature serviceability of an elastomeric product. Consequently, in designing neoprene compounds, an awareness of the effects of both transitions on the various neoprene types is essential as well as the changes in low temperature properties which occur as a result of variations in state of cure and compound formulation. Experiments were designed to study the effects of both first and second order transition independently. Through this work, the manifestations of both first and second order transition, and the effect on these properties of variations in neoprene type, compounding ingredients, and state of cure became readily apparent.

FIRST ORDER TRANSITION (CRYSTALLIZATION)

As a polymer crystallizes, segments of the molecular chains gradually become oriented with reference to each other. The progress of this orientation process has been followed by x-ray diffraction techniques. With neoprene, a well-developed crystalline structure is indicated by a sharp peak in diffraction intensity[13] at 19° 30′. As crystallization develops, a noticeable hardening, stiffening and loss of flexibility takes place. Also, a small decrease in volume occurs and stressed specimens tend to relax. However, crystallization is a completely reversible phenomenon. With the application of heat, specimens return to their original volume and degree of flexibility. Also, they recover from any relaxed condition which may have developed as a result of crystallization under stress. Crystallization rate varies with neoprene type and is de-

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pendent on exposure temperature, degree of stress, state of cure, and compounding ingredients.

Test methods.—Three procedures, as described below, were used to measure rate and extent of crystallization. In all cases, samples were heated for 30 minutes at 70° C (158° F) to remove all traces of crystallinity before determining crystallization rate at low temperatures. Measurements of the property being affected by crystallization were made at frequent and regular time intervals.

The simplest test method and the one used most frequently was the measurement of Shore A durometer hardness increase. A 3 inch × 3 inch × $\frac{1}{4}$ inch test specimen was used. Crystallization rate was determined by noting the time required for the sample to increase 20 points in durometer hardness above its value at the test temperature. The durometer was maintained at the indicated temperature throughout the test. To provide a smooth surface for hardness measurements of raw polymer, test specimens were prepared by compressing milled polymer in a chromium-plated mold for 15 minutes at 121° C (250° F). The molded neoprene was cooled under pressure to room temperature to permit easy removal from the mold.

A second and more precise method was to measure the decrease in volume which occurred as a result of crystallization. Dilatometric techniques as described by Bekkedahl[1] were employed with silicone oil (SF-81-50, General Electric Co.) as the confining fluid. Silicone oil is suitable for dilatometric studies involving neoprene as it has been found by us and by others[9] to produce no swell after prolonged exposure at room temperature. Half times of crystallization are reported when this technique was used.

A third test involved measuring crystallization rates of specimens under compressive stress. Compression set (ASTM D-1229) was determined after several different conditioning times at the selected exposure temperature. Crystallization was considered over when the specimen retained a 90% compression set after 30 minutes recovery time at the test temperature.

Neoprene type.—The commercially available neoprenes have widely different crystallization rates[2, 14]. The first experiment was designed to compare the crystallization rates at −10° C (14° F) of raw polymers and gum vulcanizates of Neoprenes GN, GRT, W, WX, WRT, and WB, using the durometer

TABLE I

GUM COMPOUNDS OF VARIOUS GENERAL PURPOSE NEOPRENES
(Figures 1 & 2)

	1-A	1-B	1-C	1-D	1-E	1-F
Neoprene W	100	—	—	—	—	—
Neoprene WB	—	100	—	—	—	—
Neoprene WX	—	—	100	—	—	—
Neoprene WRT	—	—	—	100	—	—
Neoprene GN	—	—	—	—	100	—
Neoprene GRT	—	—	—	—	—	100
Magnesia	4	4	4	4	4	4
N-phenyl-1-naphthylamine[1]	1	1	1	1	1	1
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
2-Mercaptoimidazoline[2]	0.5	0.5	0.5	0.5	—	—

Cure: 25 minutes at 153° C (307° F)

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

hardness increase method. The compounding recipes used are listed in Table I, and the crystallization rates obtained are shown in Figure 1. Neoprene W has the fastest crystallization rate of the neoprenes studied. Somewhat slower to crystallize are Neoprene WB, WX, and GN. These three neoprenes have appreciably faster crystallization rates than Neoprene GRT. However, Neoprene WRT is by far the most crystallization resistant type.

Vulcanization retards the crystallization rate of neoprene but it does not change the order of the various types. The magnitude of change in rate does vary, however, depending on type. For example, at −10° C (14° F) Neoprene W when cured becomes about five times more crystallization resistant while Neoprene WRT becomes ten times more resistant. For comparison, natural rubber at 2° C becomes about six times more crystallization resistant when cured[17].

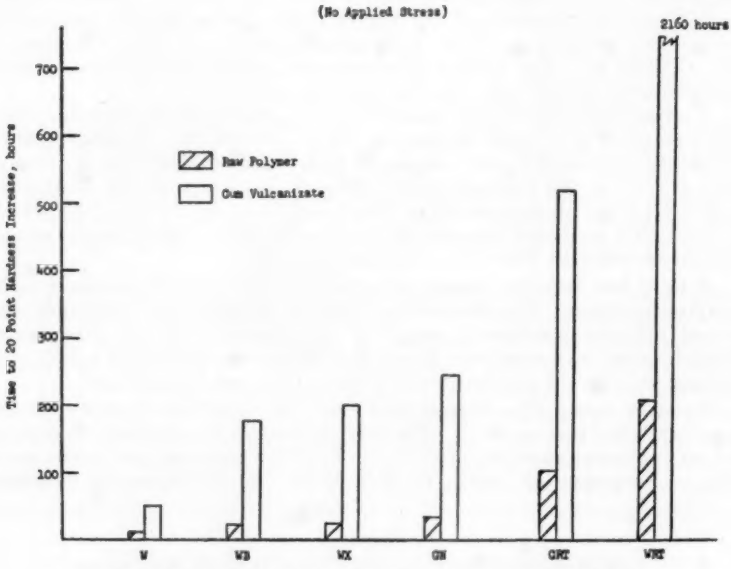

FIG. 1.—Crystallization rates of raw neoprene polymers and gum vulcanizates at −10° C.

The very rapid crystallizing neoprenes (Neoprenes CG, AC, and AD), which are especially designed for adhesive applications, could not be tested at −10° C (14° F) since the 20 point increase in hardness occurred before the specimens reached thermal equilibrium at the test temperature.

The crystallization rates of various neoprene types under stress were compared by measuring compression set after exposing the vulcanizates for various time intervals at −10° C (14° F). Vulcanizates of Neoprene Types W, WRT, GN, and GRT (Compounds 1-A, 1-D, 1-E, and 1-F) were studied. The test results plotted in Figure 2 show once again that Neoprene W crystallizes most rapidly, followed by GN, GRT, and WRT. In all cases, crystallization rate was increased considerably due to the applied stress. For example, the Neoprene WRT vulcanizate crystallized in 400 hours (16.5 days) at −10° C (14° F)

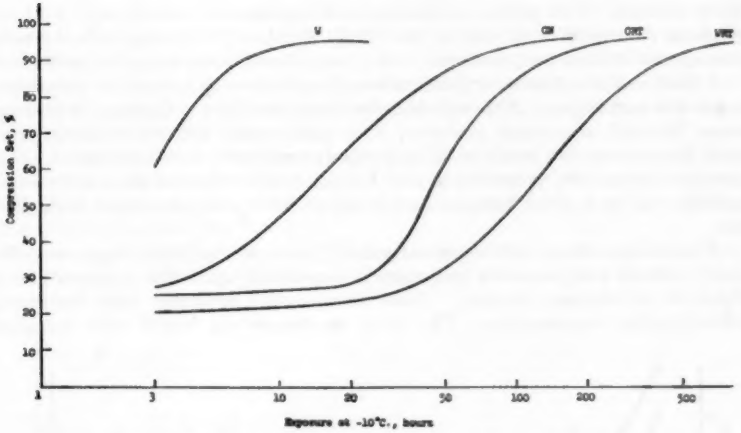

FIG. 2.—Crystallization rate of neoprene vulcanizates under compressive stress.

when under compressive stress compared with 2160 hours (90 days) when no applied stress was used as shown in Figure 1.

Optimum crystallization temperature.—At temperatures below the melting point, both the nucleation rate and growth rate of polymer crystals are temperature dependent[11]. The nucleation rate is favored thermodynamically by relatively low temperatures. Conversely, the growth rate of crystals is favored by relatively higher temperatures which permit greater molecular mobility. Consequently, at some intermediate temperature, crystallization is completed most rapidly, since favorable conditions exist for both crystal initiation as well as crystal growth.

The temperature at which neoprene vulcanizates crystallize most rapidly was determined. The Neoprene W and Neoprene GN compounds chosen for this study are shown in Table II. Dilatometric determinations of crystallization rates were made at 0°, −5°, −10°, −15° and −20° C. Times to half crystallization at the five temperatures are shown in Figure 3. Again Neoprene W crystallized much faster than Neoprene GN throughout the range of temper-

TABLE II

COMPOUNDS USED TO DETERMINE OPTIMUM CRYSTALLIZATION TEMPERATURE
(Figure 3)

	2-A	2-B
Neoprene W	100	—
Neoprene GN	—	100
N-phenyl-1-naphthylamine[1]	2	2
Magnesia	4.0	4.0
Stearic acid	0.5	0.5
SRF carbon black	29.0	29.0
Zinc oxide	5.0	5.0
2-Mercaptoimidazoline[2]	0.5	—
Cure: 25 minutes at 153° C (307° F)		

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

atures studied. This plot shows that crystallization rate is most rapid for both neoprene vulcanizates at −12° C (+10° F) which is 7° C lower than the optimum cyrstallization temperature of −5° C reported for raw neoprene polymers[9].

A shift in the optimum crystallization temperature as a result of vulcanization is not surprising. Although the chemical crosslinks introduced would decrease internal segmental mobility, they also would depress melting point much the same as if a noncrystallizing copolymeric unit were introduced. Apparently the melting point depression has a greater influence than decrease in mobility and so a lower temperature is required for a rapid crystal nucleation rate.

Thaw temperature.—Other investigators[12] have shown that the thaw point of crystallized neoprene raw polymers is dependent upon the temperature at which the crystals are formed. Thaw temperature decreases with decreasing crystallization temperature. This same tendency was noted with neoprene

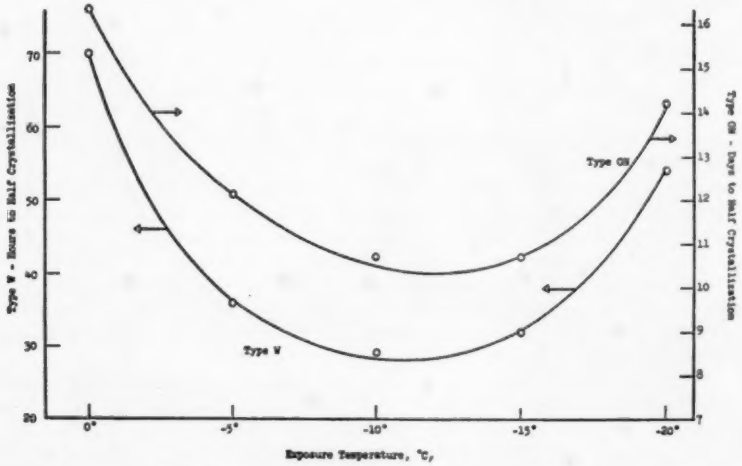

FIG. 3.—Effect of temperature on crystallization rate.

vulcanizates as illustrated in Figure 4. Three Neoprene W specimens were prepared by mixing stock according to formulation 1-A and curing for 25 minutes at 153° C (307° F). They were allowed to crystallize at −10° C (14° F). As crystallization occurred, the durometer hardness of the specimens gradually increased to 92 after 120 hours. Then the three crystallized specimens were removed from the −10° C cold box and immediately placed in warmer environments. One sample was exposed at 0° C (32° F). Within one hour its hardness decreased from 92 to 80, indicating some thawing had taken place at the warmer temperature. At this point the specimen began to increase in hardness again until it reached a value of 88 after an additional 100 hours exposure. Obviously, the 0° C (32° F) temperature was favorable for crystallization.

The second sample was immediately placed in a +5° C cold box after removal from the −10° C box. The hardness of this sample decreased from 92 to 65 in less than 1 hour before gradually increasing once again and after 200 hours

reached a value of 82. This second sample was then removed from the +5° C box and warmed to 18° C. After 30 minutes, the specimen decreased in hardness to within two points of its original value, showing that the 13° C increase in temperature caused essentially all the crystals to thaw. Subsequent exposure of the sample to the relatively warm +18° C temperature resulted in only a 17 point rise after 112 days.

The third sample, which was crystallized at −10° C (14° F), was transferred to an environment of +10° C (50° F). This 20° C change in temperature was sufficient to cause complete decrystallization as shown by the drop in hardness to the original value of 45.

It was concluded that the temperature at which a neoprene vulcanizate is crystallized determines the minimum temperature at which it will thaw, the

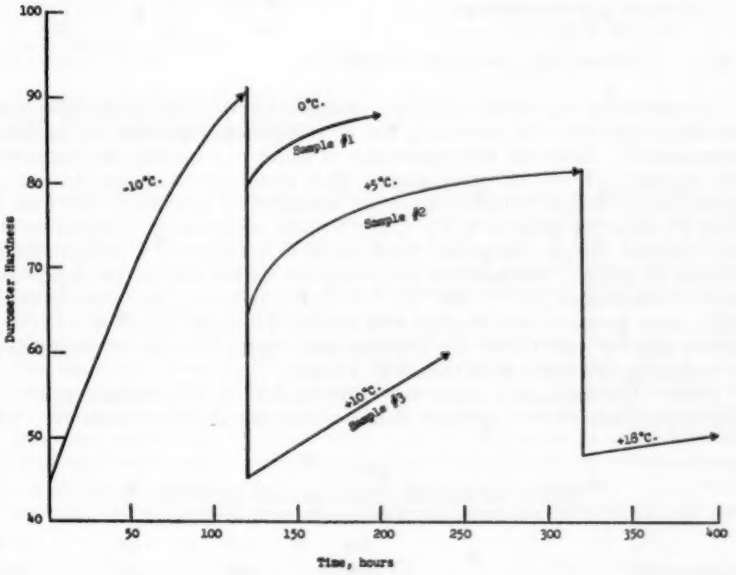

FIG. 4.—Thaw point as a function of crystallization temperature.

thaw point being approximately 15° C higher (over the range studied) than the temperature at which the neoprene was crystallized.

State of cure.—Earlier it was shown that vulcanization improved markedly neoprene's resistance to crystallization. Accordingly, it follows that increased state of cure should retard crystallization. Three vulcanizates were prepared by curing a Neoprene GN compound 10, 20 and 40 minutes, respectively, at 153° C (307° F). The cured compounds were tested for stress-strain properties and crystallization rate using the dilatometer method. The test compound and vulcanizate properties are shown in Table III. By increasing cure time from 10 to 40 minutes, stress at 300% strain increased from 1200 to 1500 pounds per square inch. Accompanying this increase in state of cure, half time for crystallization increased from 190 to 370 hours.

TABLE III

EFFECT OF STATE OF CURE ON CRYSTALLIZATION RATE

Base Compound			
Neoprene GN		100	
N-phenyl-1-naphthylamine[1]		2	
Magnesia		4	
Stearic acid		0.5	
SRF carbon black		29.0	
Zinc oxide		5.0	
Cure time (minutes) at 153° C (307° F)	10	20	40
Stress at 300% elongation, psi	1200	1350	1500
Tensile strength, psi	2650	2700	2700
Elongation, %	680	610	580
Hardness, durometer	62	63	64
Hours to half crystallization at −10° C (14° F)	190	270	370

[1] Neozone A—E. I. du Pont de Nemours & Co.

Compounding ingredients.—Sulfur. Sulfur is known to be a beneficial compounding ingredient for increasing the crystallization resistance of neoprene vulcanizates[6]. However, the importance of sulfur in retarding crystallization rate appears to be considerably greater than would be anticipated from consideration of its effect on state of cure as measured by modulus. The data in Table IV show the effect of 0, 0.5, 1, and 2 parts, respectively, of sulfur on the time required for the durometer hardness of a Neoprene GN vulcanizate to increase 20 points. Stress-strain properties are shown also for the compound cured 40 minutes at 153° C (307° F). With this relatively long cure, stress at 400% strain increased only slightly with increased amounts of sulfur. Crystallization time at −10° C (14° F), however, was delayed from 14 days to 69 days by increasing the sulfur level from 0 to 2 parts.

Filler. Crystallization rates were determined for five vulcanizates containing 40 volumes of five different fillers per 100 volumes of Neoprene W. The

TABLE IV

EFFECT OF SULFUR CONCENTRATION ON STATE OF CURE AND CRYSTALLIZATION RATE

	4-A	4-B	4-C	4-D
Neoprene GN	100	100	100	100
N-phenyl-1-naphthylamine[1]	2	2	2	2
Magnesia	4	4	4	4
Stearic acid	0.5	0.5	0.5	0.5
MT carbon black	58	58	58	58
Aromatic petroleum oil	10	10	10	10
Zinc oxide	5	5	5	5
Sulfur	—	0.5	1.0	2.0
Cure: 40 min at 153° C (307° F)				
Stress at 400%, psi	1300	1375	1400	1425
Tensile strength, psi	1875	1800	1950	1850
Elongation, %	780	740	720	660
Hardness	58	60	61	62
Days for 20 point increase in hardness @ −10° C (14° F)	14	36	54	69

[1] Neozone A—E. I. du Pont de Nemours & Co.

TABLE V

EFFECT OF FILLER TYPE ON CRYSTALLIZATION RATE

	5-A	5-B	5-C	5-D	5-E
Neoprene W	100	100	100	100	100
N-phenyl-1-naphthylamine[1]	1	1	1	1	1
Stearic acid	0.5	0.5	0.5	0.5	0.5
Magnesia	4.0	4.0	4.0	4.0	4.0
SRF carbon black	58.5	—	—	—	—
MT carbon black		58.5	—	—	—
Calcium carbonate[2]	—	—	88	—	—
Hard clay	—	—	—	83.5	—
Precipitated silicon dioxide[3]	—	—	—	—	62.3
Zinc oxide	5	5	5	5	5
2-Mercaptoimidazoline[4]	0.5	0.5	0.5	0.5	0.5
Cure: 25 min at 153° C (307° F)					
Hours to half crystallization at −10° C (14° F)	46	52	40	36	52

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Atomite Whiting—Thompson Weinmann & Co.
[3] HiSil 233—Columbia-Southern Chemical Corp.
[4] Na-22—E. I. du Pont de Nemours & Co.

fillers studied included SRF carbon black, MT carbon black, calcium carbonate, hard clay, and precipitated silicon dioxide. The compositions used and the results of dilatometer crystallization tests made at −10° C (14° F) are shown in Table V. All five vulcanizates had half times of crystallization of between 36 and 52 hours and no correlation seems evident between filler chemical or physical properties and crystallization rate.

Eight Neoprene W compositions containing increasing amounts of MT carbon black are shown in Table VI. These compounds, which vary in neoprene content from 93.6 to 31.3 per cent by volume, were prepared to study the effect of filler concentration on first order transition. An aromatic petroleum oil was necessary in the last four compounds of this series in order that the stocks could be processed. It will be noted in Figure 5 that the volume change decreases linearly as the volume per cent neoprene is decreased. This linear relationship would be expected since the neoprene is the only significant part

TABLE VI

COMPOUNDS USED TO DETERMINE EFFECT OF FILLER CONCENTRATION ON CRYSTALLIZATION RATE (Figure 5)

	6-A	6-B	6-C	6-D	6-E	6-F	6-G	6-H
Neoprene W	100	100	100	100	100	100	100	100
N-phenyl-1-naphthylamine[1]	2	2	2	2	2	2	2	2
Magnesia	4	4	4	4	4	4	4	4
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MT carbon black	—	7.3	29.7	58.5	87.7	117.0	146.4	204
Aromatic petroleum oil	—	—	—	—	8.0	16.0	26.0	54
Zinc oxide	5	5	5	5	5	5	5	5
2-Mercaptoimidazoline[2]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Per cent by volume Neoprene	93.6	89.2	78.7	68.0	56.3	48.0	41.4	31.3

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

of the formulation subject to crystallization. However, quite unexpectedly it was observed that crystallization rate remained essentially constant until the per cent by volume neoprene was decreased below 55%. With further reduction in neoprene content, time to half crystallization increased sharply. This might be attributed to the aromatic petroleum oil used in these heavily loaded stocks (see below).

Plasticizer type.—Crystallization rate is influenced considerably by the type of plasticizer used in a compound. Certain polymeric hydrocarbons derived from petroleum oil or coal tar have been shown to retard first order transition[13]. During the course of our investigation it was found that other plasticizers, such as esters, increase crystallization rate. A comparison of the crystallization

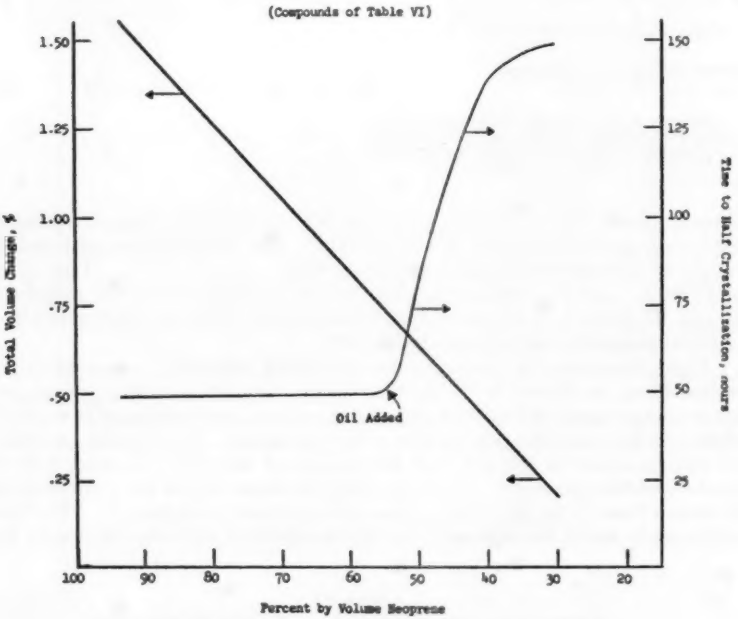

FIG. 5.—Effect of filler concentration on degree and rate of crystallization.

rates of three Neoprene W compounds containing 15 parts of three different plasticizer types (light naphthenic petroleum oil, resinous petroleum hydrocarbons and an ester) and a control containing no plasticizer, was made at −10° C (14° F). The formulations and results of crystallization tests (dilatometer and durometer hardness) are given in Table VII. The vulcanizate containing a light petroleum oil (7-B) had a crystallization rate very close to that of the unplasticized control (7-A). When 15 parts of a resinous petroleum hydrocarbon was used in place of an equivalent amount of petroleum oil (7-C versus 7-B), approximately a sixfold *decrease* in crystallization rate was measured. With 15 parts of butyl oleate, about a fourfold *increase* in crystallization rate resulted (7-D versus 7-B). This acceleration of crystallization is

TABLE VII

EFFECT OF PLASTICIZER CLASS ON CRYSTALLIZATION RATE

	7-A	7-B	7-C	7-D
Neoprene W	100	100	100	100
N-phenyl-1-naphthylamine[1]	2	2	2	2
Magnesia	4	4	4	4
Stearic acid	0.5	0.5	0.5	0.5
SRF carbon black	58.5	58.5	58.5	58.5
Light naphthenic petroleum oil	—	15	—	—
Resinous petroleum hydrocarbon[2]	—	—	15	—
Butyl oleate	—	—	—	15
Zinc oxide	5	5	5	5
2-Mercaptoimidazoline[3]	0.5	0.5	0.5	0.5
Cure: 25 minutes at 153° C (307° F)				
Crystallization tests at −10° C (+14° F)				
Dilatometer method				
Hours to half crystallization	44	38	220	10
Durometer hardness method				
Hours to a 20 point increase @ −10° C (14° F)	48	40	264	11

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Kenflex A—Kenrich Corporation.
[3] Na-22—E. I. du Pont de Nemours & Co.

believed to be due to the ester favoring greater freedom of molecular motion which facilitates rapid crystal growth.

Since butyl oleate increased crystallization rate at −10° C (14° F), it was decided to determine its effect on crystallization at other temperatures as well. Testing temperatures ranging from +10° C to −43° C were investigated. The formulations used are shown in Table VIII. Two controls were included: one was prepared from Neoprene W using 20 parts of petroleum oil (8-B) and the other was prepared using 20 parts of butyl oleate in Neoprene WRT (8-C).

TABLE VIII

EFFECT OF LOW TEMPERATURE PLASTICIZER ON CRYSTALLIZATION RATE AT VARIOUS TEMPERATURES
(See Figure 6)

	8-A	8-B	8-C
Neoprene W	100	100	—
Neoprene WRT	—	—	100
Magnesia	4	4	4
N-phenyl-1-naphthylamine[1]	2	2	2
SRF carbon black	58	58	58
Butyl oleate	20	—	20
Aromatic petroleum oil	—	20	—
Zinc oxide	5	5	5
2-Mercaptoimidazoline[2]	0.5	0.5	0.5
Cure: 25 minutes at 153° C (307° F)			
Young's Modulus @ −40° F., ASTM D-797			
Original	1,960	11,000	1,240
After 3 days	14,000	15,000	2,000

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

It can be seen in Figure 6 that butyl oleate increased crystallization rate of Neoprene W over the entire temperature range studied. Crystallization of the W vulcanizate containing butyl oleate (8-A) was nearly as fast at −25° C (−13° F) as at −10° C (+14° F), illustrating that with ester plasticizer present a much broader temperature range exists at which crystallization is highly favorable. In fact, even at −43° C, Neoprene W with ester present (8-A) has a half time of crystallization of only 96 hours. Further evidence of crystallization at very low temperatures with ester present is shown by Young's Modulus stiffness data (ASTM D-797) in Table VIII. The Neoprene W vulcanizate containing butyl oleate (8-A) increased markedly in stiffness in only three days at −40° C while Neoprene W with petroleum oil (8-B) and the

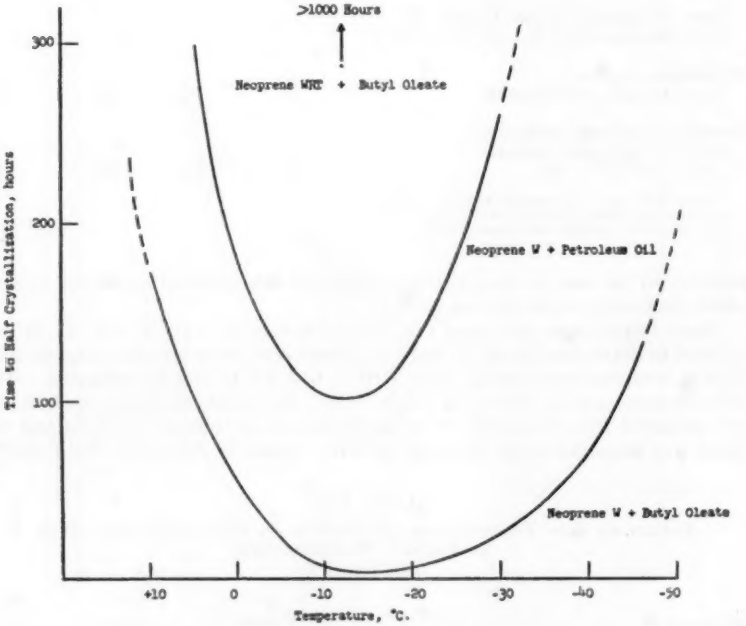

FIG. 6.—Effect of plasticizer type on crystallization rate.

Neoprene WRT vulcanizate containing butyl oleate (8-C) increased relatively little in stiffness. If butyl oleate had become incompatible with time of exposure at this low temperature, the WRT stock would have stiffened considerably also. This indicates that delayed stiffening at extremely low temperatures results from crystallization favored by the presence of ester plasticizer rather than phasing out of the plasticizer due to incompatibility as previously believed[7].

Low temperature plasticizer concentration.—The effect of low temperature plasticizer concentration on crystallization rate was examined. Neoprene WRT formulations containing 0, 10, 20, 30, and 40 parts, respectively, of butyl oleate were selected for this work. The compounds and results of durometer

TABLE IX

EFFECT OF LOW TEMPERATURE PLASTICIZER CONCENTRATION

	9-A	9-B	9-C	9-D	9-E
Neoprene WRT	100	100	100	100	100
Magnesia	4	4	4	4	4
N-phenyl-1-naphthylamine[1]	2	2	2	2	2
SRF carbon black	58	58	58	58	58
Zinc oxide	5	5	5	5	5
2-Mercaptoimidazoline[2]	0.5	0.5	0.5	0.5	0.5
Butyl oleate	—	10	20	30	40
Cure: 30′/153° C (307° F)					
Hours for 10 point increase in durometer hardness @ −10° C (14° F)	1680	980	646	484	360

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

hardness increase measurements at −10° C (14° F) on this series of vulcanizates are given in Table IX. In each case the time for a 10 point increase in durometer hardness rather than the usual 20 point increase was reported. This was done because the vulcanizate containing no plasticizer (9-A) had a hardness value of 80 before crystallizing. By using only a 10 point hardness increase as a criterion of crystallization, no hardness determination had to be made above 90 where the accuracy of the Shore A hardness gauge is less reliable. The crystallization data given in Table IX show that as butyl oleate concentration is increased from 0 to 40 parts, a continual increase in crystallization rate occurs. it is pointed out that Compound 9-E, containing 40 parts of butyl oleate, still possessed a high degree of crystallization resistance because of the inherent crystallization resistance of Neoprene WRT. Durometer hardness increased only 10 units in 364 hours (15 days) at the highly favorable crystallization temperature of −10° C (14° F).

Effect of crystallization on brittleness.—The effect of crystallization on brittleness temperature was determined. The compounds of Table X cured for 20 minutes at 153° C (307° F) were allowed to crystallize for one week at −10° C

TABLE X

EFFECT OF CRYSTALLIZATION ON BRITTLENESS TEMPERATURE

	10-A	10-B
Neoprene W	100	100
Magnesia	4	4
N-phenyl-1-naphthyalmine[1]	2	2
SRF carbon black	58	58
Aromatic petroleum oil	25	—
Butyl oleate	—	25
Zinc oxide	5	5
2-Mercaptoimidazoline[2]	0.5	0.5
Cure: 30′/153° C (307° F)		
Brittleness Temperature (ASTM D-746)		
Uncrystallized specimen	−41° C	−68° C
Specimen crystallized for 1 week at −10° C (14° F)	−40° C	−69° C

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.

(14° F). This exposure was at least three times greater than was required for the Type W vulcanizates to crystallize. Without removing the crystallized specimens from the −10° C (14° F) cold box, the samples were placed in −70° C (−94° F) acetone and transferred to a brittleness tester, maintained at −70° C. Brittleness tests (ASTM D-746) were run on the crystallized specimens as well as on uncrystallized samples of the same vulcanizates. The results of these tests (Table X) confirm previous findings[10] that the process of crystallization does not change the brittleness temperature of a neoprene vulcanizate.

BEHAVIOR OF NEOPRENE UNDER SHORT-TERM LOW TEMPERATURE CONDITIONS

Neoprene, like all elastomers, becomes progressively stiffer by exposing it to successively lower temperatures. This effect, unlike crystallization, is

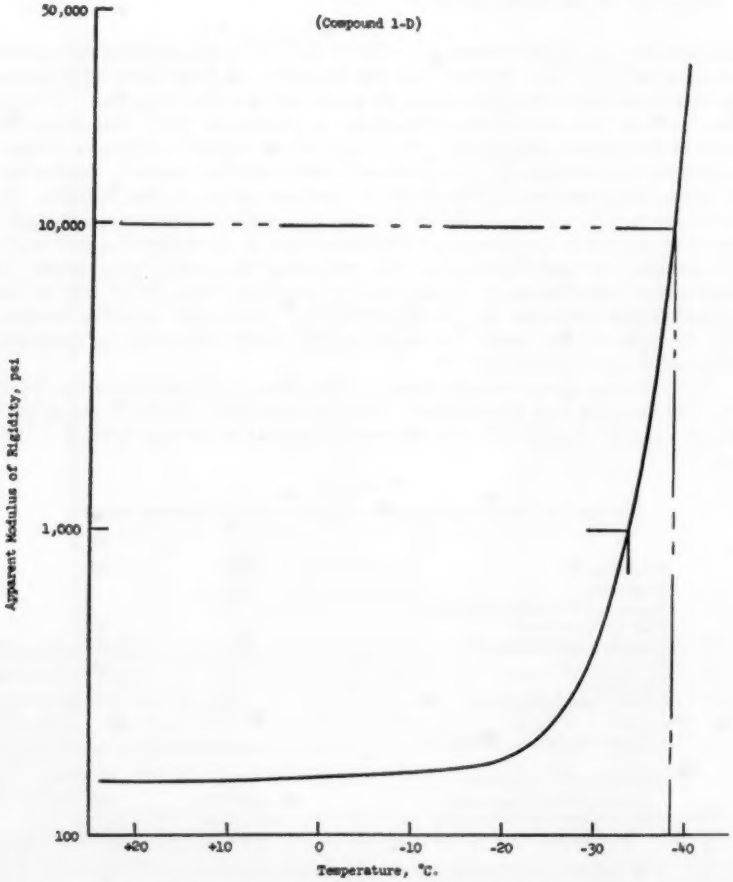

FIG. 7.—Effect of temperature on stiffness of WRT gum vulcanizate.

evident just as soon as thermal equilibrium is established. To illustrate this point, an unreinforced Neoprene WRT vulcanizate (Compound 1-D) was cooled in 10° C increments and, after thermal equilibrium was established, torsional stiffness tests (ASTM D-1043) were made. Neoprene WRT was used in order to make certain that crystallization was not affecting the stiffness measurements. The unplasticized Neoprene WRT vulcanizate suddenly became exceedingly stiff when its temperature was reduced to approximately −35° C as shown in Figure 7. Stiffness increased by a factor of 10, from 2000 psi to 20,000 psi, as temperature was decreased from −35° C to −39° C. This rapid increase in stiffness is associated with second order transition of the polymer phase. Very accurate measurements of second order transition (glass) temperature can be determined by refractive index, specific heat or thermal coefficient of expansion measurements[16]. However, some investigators have preferred to consider as a practical index of service-ability the temperature at which a material reaches a certain degree of stiffness[8, 10]. The index used by

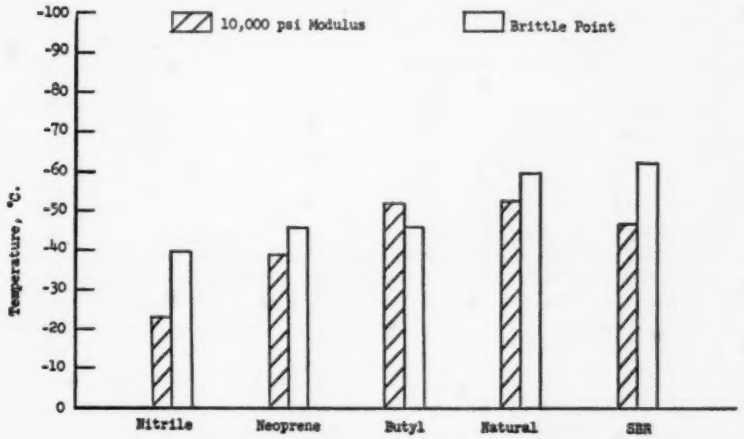

FIG. 8.—Brittle point and 10,000 PSI modulus temperature for various elastomers.

Liska[10] and for the work reported herein, was the temperature at which the vulcanizate reached an apparent modulus of rigidity of 10,000 psi. In the case of an unreinforced, unplasticized Neoprene WRT vulcanizate, Figure 6 shows that a 10,000 psi modulus (ASTM D-1043) was obtained at −38° C.

At very low temperatures, a specimen becomes brittle and will shatter on sudden bending or impact. The temperature at which this occurs depends on the rate of application of load and specimen thickness. When determined under certain prescribed testing conditions, such as ASTM D-746, this temperature is called the brittleness temperature of the composition. The brittleness temperature bears no direct relationship to stiffness as shown in Figure 8. Brittleness temperature (ASTM D-746) and 10,000 psi stiffness determinations were made for vulcanizates of five different elastomers (neoprene, styrene-butadiene, nitrile, butyl, and natural rubber). All but the butyl vulcanizate had a lower brittleness temperature than the 10,000 psi stiffness temperature. However, the temperature difference between brittleness temperature and 10,000

TABLE XI

COMPARISON OF BRITTLE POINT AND 10,000 PSI STIFFNESS TEMPERATURE OF UNREINFORCED NEOPRENE VULCANIZATES
(Compounds Shown in Table I)

Compound number	Neoprene type	Cure at 153° C (307° F)	ASTM D-1043 10,000 psi stiffness temp, ° C	ASTM D-746 brittle temp, ° C
1-A	W	15	−42	−42
1-C	WX	15	−40	−41
1-B	WB	15	−40	−40
1-E	GN	7½	−39	−41
1-E	GN	15	−39.5	−41
1-E	GN	30	−38.5	−41
1-F	GRT	15	−38.0	−40
1-D	WRT	15	−37.5	−39

psi stiffness temperature varied considerably among the elastomers tested. This lack of relationship between stiffness and brittleness is not surprising inasmuch as stiffness measurements involve loading at low speed and low deflection, while brittleness tests involve impact loading at high speed and high deflection.

Neoprene type and state of cure.—Brittleness temperature (ASTM D-746) and torsional stiffness (ASTM D-1043) measurements were made on the unreinforced vulcanizates of Table I to determine the effect of neoprene type on these properties. In addition, the effect of state of cure on Neoprene GN was determined by testing three samples of Compound 1-E cured 7.5, 15, and 30 minutes, respectively, at 153° C (307° F).

The results of these short-term exposure tests at low temperatures are given in Table XI. Brittleness and 10,000 psi stiffness temperatures increase slightly with neoprenes of increasing crystallization resistance but the variation is within a 5° C range. Also, the brittleness temperature is slightly lower than

TABLE XII

EFFECT OF FILLER TYPE AND CONCENTRATION ON 10,000 PSI STIFFNESS AND BRITTLENESS TEMPERATURE

Neoprene W	100
N-phenyl-1-naphthylamine[1]	2
Maglite D	4
Filler	As shown
Zinc oxide	5
2-Mercaptoimidazoline[2]	0.5

Compound number	Filler	Concentration parts	ASTM D-1043 10,000 psi stiffness temp, ° C	ASTM D-746 brittle temp, ° C
12-A	None	—	−42	−42
12-B	MT carbon black	20	−40	−42
12-C	MT carbon black	40	−39	−42
12-D	MT carbon black	80	−38.5	−42
12-E	SRF carbon black	40	−37.5	−45
12-F	Hard clay	40	−39.5	−41
12-G	Calcium carbonate[3]	40	−39.5	−38

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.
[3] Atomite Whiting—Thompson Weinmann & Co.

TABLE XIII

EFFECT OF PLASTICIZER CLASS ON 10,000 PSI STIFFNESS AND BRITTLENESS TEMPERATURE

Compound	Plasticizer	Parts	ASTM D-1043 10,000 psi stiffness temp, ° C	ASTM D-746 brittle temp, ° C
13-A (7-A)	None	—	−38	−44
13-B (7-B)	Light naphthenic petroleum oil	15	−42	−46
13-C (7-C)	Resinous petroleum hydrocarbon[1]	15	−31	−34
13-D (7-D)	Butyl oleate	15	−53	−61

[1] Kenflex A—Kenrich Corporation.

the 10,000 psi stiffness temperature in all cases except for Neoprene W and Neoprene WB. Although increased state of cure was shown previously to have a considerable retarding effect on crystallization rate, it has essentially no effect on brittleness or 10,000 psi stiffness temperatures.

Filler type and concentration.—Brittleness and stiffness measurements of vulcanizates containing 40 parts of four different fillers (MT carbon black, SRF carbon black, hard clay, and calcium carbonate) and three different concentrations of MT carbon black (20, 40, and 80 parts) were determined. The formulations and test results are shown in Table XII. Although brittleness temperature was unaffected by increasing the MT carbon black loading from 0 to 80 parts, a slight increase in the 10,000 psi stiffness temperature was noted with increasing filler concentration. By contrast, variations in filler type produced no significant differences in stiffness temperature but had a noticeable effect on brittleness temperature. The vulcanizate containing 40 parts SRF carbon black had the lowest brittleness temperature (−45° C), while the one containing 40 parts calcium carbonate had the highest brittleness temperature (−38° C).

TABLE XIV

EFFECT OF LOW TEMPERATURE PLASTICIZER TYPE ON 10,000 PSI STIFFNESS AND BRITTLENESS TEMPERATURE

Neoprene	
Neoprene W	100
Magnesia	4
N-phenyl-1-naphthylamine[1]	2
SRF carbon black	58
Zinc oxide	5
2-Mercaptoimidazoline[2]	0.5
Plasticizer (as shown)	20

Compound	Plasticizer	ASTM D-1043 10,000 psi stiffness temp, ° C	ASTM D-746 Brittle temp, ° C
14-A	Butyl oleate	−54	−62
14-B	Dioctyl sebacate	−56	−56
14-C	Polyether[3]	−55	−58
14-D	Trioctyl phosphate	−56	−56

[1] Neozone A—E. I. du Pont de Nemours & Co.
[2] Na-22—E. I. du Pont de Nemours & Co.
[3] TP 90B—Thiokol Chemical Corporation.

Plasticizer type.—Both low temperature stiffness and brittleness are influenced considerably by the class of plasticizer used, as shown in Table XIII. When 15 parts of a light naphthenic petroleum oil were added to a Neoprene W compound containing 58 parts SRF carbon black, both the 10,000 psi stiffness and brittleness temperatures decreased a few degrees. However, the replacement of 15 parts of petroleum plasticizer with a resinous petroleum hydrocarbon caused an 11° C increase in 10,000 psi stiffness temperature and a 12° C rise in brittleness temperature. With the ester plasticizer, butyl oleate, the reverse effects were noted. An 11° C decrease in stiffness temperature and 15° C decrease in brittleness temperature resulted from the substitution of 15 parts of butyl oleate for 15 parts of petroleum oil.

Because butyl oleate is very effective in reducing both the brittleness and second order transition temperatures of neoprene vulcanizates, this ester plasticizer is used frequently in neoprene products which must perform well at extremely low temperatures. Three other low temperature plasticizers which also improve these properties in neoprene include dioctyl sebacate, a polyether, and trioctyl phosphate. The effectiveness of 20 parts of each of the above plasticizers in reducing the 10,000 psi stiffness and brittleness temperatures of Neoprene WRT is shown in Table XIV. Although all four plasticizers depressed the 10,000 psi stiffness temperature to about the same extent, butyl oleate was somewhat more effective than the other three in reducing brittleness temperature.

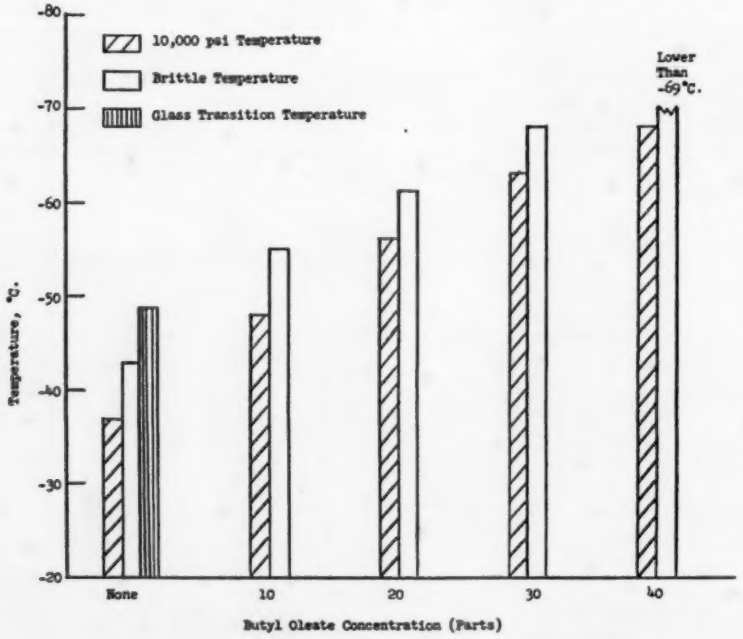

FIG. 9.—Effect of low temperature plasticizer concentration on glass transition, 10,000 psi stiffness and brittle temperature.

Low temperature plasticizer concentration.—Determination of the effect of a stepwise increase in low temperature plasticizer concentration on short-term, low temperature properties was undertaken. The Neoprene WRT compounds of Table IX which contained 0, 10, 20, 30 and 40 parts, respectively, of butyl oleate, were cured for 30 minutes at 153° C (307° F). In addition to the usual tests, a more precise second order transition or glass temperature was determined on the unplasticized vulcanizate (9-A). This was done by following a procedure similar to that used by Dannis[3] involving the measurement of the change in length of a $\frac{1}{4}''$ thick pellet with temperature and noting the temperature at which the coefficient of thermal expansion abruptly changed. The low temperature test results are shown in Figure 9. As the concentration of butyl oleate was increased, 10,000 psi stiffness and brittleness temperatures decreased. In all cases, brittleness temperature was lower than the 10,000 psi stiffness temperature. The unplasticized vulcanizate had a glass (second order transition) temperature 12° C lower than the 10,000 psi stiffness temperature. This relationship between low temperature stiffness and glass temperature agrees well with the findings of Trick[15] who recently reported that this difference is approximately 15° C for eight other elastomers.

SUMMARY

Neoprene vulcanizates crystallize most rapidly at −12° C. The temperature at which a vulcanizate is crystallized determines the minimum temperature at which it will thaw, the thaw point being approximately 15° C higher than the crystallization temperature over the range studied. Brittleness temperature is not changed as a result of crystallization. Crystallization resistance of the general purpose dry neoprene types increases in the following order: W, WB, WX, GN, GRT, WRT. Depending on the neoprene type, crystallization is retarded by a factor of 5 to 10 by vulcanization. Variation of filler type does not change crystallization rate appreciably. Crystallization rate is retarded through the use of sulfur, certain resinous type plasticizers, as well as by increased state of cure. Ester plasticizers which depress brittleness tempterature and reduce stiffening at low temperatures increase crystallization rate considerably and permit crystallization to occur at very low temperatures. Brittleness and 10,000 psi stiffness temperatures are not affected appreciably by neoprene type, state of cure, or amount and type of filler. Glass transition is approximately 12° C lower than the 10,000 psi stiffness temperature and 6° C lower than the brittleness temperature.

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THE OXIDATIVE AGING IN ULTRAVIOLET LIGHT OF DICUMYL PEROXIDE VULCANIZATES OF NATURAL RUBBER IN PRESENCE OF VARIOUS ANTIOXIDANTS *

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The oxidative aging of natural rubber vulcanizates at 25° C under irradiation by ultraviolet light of wavelength 365 mμ has been described in a number of communications from this laboratory. At this wavelength naphthylamines were shown to accelerate degradation of peroxide vulcanizates while substituted *p*-phenylenediamines inhibited it[1]; α-naphthol[2] and a variety of dithiocarbamates[3] were also found to have a protective action. Since some amines and phenolic antioxidants do not absorb light of wavelength 365 mμ but do absorb in the region of 313 mμ, investigations have now been made of the effect of a large number of additives on aging at the shorter wavelength, so that predictions might be made of the most suitable materials to employ in protecting unfilled vulcanizates against crazing in sunlight.

EXPERIMENTAL

APPARATUS

Aging was followed by measurement of stress relaxation by means of an instrument similar to that described by Berry, modified so that it could be automatically operated[4]. The tension in a strip, 3 × 0.5 × 0.02 cm, of the vulcanizate held at 100% extension was balanced by the force in a helical steel spring whose extension could be measured by a vernier on the side of the relaxometer. At the point of balance an electrical circuit was completed through a contact on the upper specimen clamp and one on the body of the relaxometer.

TABLE I

Wavelength, mμ	Energy, watts/steradian	Transmission, %
366.5	1.1	86
334	0.46	80
313.5	0.49	62
303	0.30	42

By means of a relay, completion of this circuit caused the vernier screw to be rotated through 360° by a rotary solenoid (Ledex by National Switch Factory Ltd.) and also caused a mark to be made on the chart of an operations recorder (Evershed & Vignoles Ltd.). Each turn of the head represented a decrease of 0.104 in the vernier reading, and if the initial vernier reading was known, the reading at the times marked on the chart was readily calculated. The results were plotted as graphs of log f/f_0 against time in the usual way.

* Reprinted from the *Journal of Applied Polymer Science*, Vol. 4, pages 151–158 (1960).

The light from a compact source lamp (250-w ME/D type of British Thomson Houston Ltd.) was filtered only by the Pyrex jacket in which the relaxometer was placed; the energy output of the principal ultraviolet mercury lines, according to the manufacturers, and their percentage transmission by the Pyrex jacket are shown in Table I. The relaxometer was irradiated in air in a thermostat maintained at 25° C.

MATERIALS

In all the experiments described, acetone-extracted highly purified rubber (U. S. Rubber Co.), vulcanized with 3% dicumyl peroxide for 35 minutes at 140° C, was employed. Sheets of vulcanizate 0.2 mm thick were obtained by use of a special mold. These were extracted with hot acetone for 24 hours, dried, and stored *in vacuo* before use.

Additives were introduced into strips of vulcanizate by swelling in the appropriate ethyl acetate solutions overnight and drying *in vacuo*. Concentrations of additives quoted below are those of the swelling solutions of which the rubber imbibed approximately its own weight.

The amines and phenols employed were commercial rubber antioxidants whose source will be noted at the appropriate point in the text. Many of the amines were purified as described previously[1]. The preparation and purification of dibutyl dithiocarbamates and diisopropyldithiophosphates has also been described elsewhere[3,5]. The isopropylxanthates were prepared by double decompositon between metal salts and potassium isopropylxanthate prepared by the method of Bulmer and Mann[4], and they were purified by recrystallization from acetone. The ultraviolet absorbers were commercial products, Tinuvin P being marketed by Geigy Ltd., U.V.9, U.V.24, and U.V.314, by the Cyanamid Co., and M.D.738 by Armour Hess Chemicals Limited.

RESULTS

AMINES

As was observed in 365 mμ light, peroxide vulcanizates containing phenyl-α-naphthylamine (PAN), phenyl-2-naphthylamine (PBN), α,β-dinaphthylamine and β,β-dinaphthylamine all degraded initially more rapidly than the control sample (Figure 1). However, at the concentration employed (1.4×10^{-3} moles amine/mole rubber) the additives had a marked protective effect in the later stages of degradation. With PAN and α,β-dinaphthylamine this effect manifested itself after about 10% loss of the original network, while with PBN and β,β-dinaphthylamine 20% of the network had degraded before the relaxation rate slowed down. Once again, the initial degradative effect of PBN was found to be most serious at a PBN concentration of 0.7×10^{-3} moles PBN/mole rubber (Figure 2). The subsequent inhibitory effect became more marked as the amine concentration was increased. At 0.35×10^{-3} moles PBN/mole rubber, the inhibition persisted only for 50 minutes, after which the relaxation rate increased again. During the inhibition period the strips were highly colored, but in those samples where the inhibition period was past, the strips had become colorless once again.

On irradiation with wavelengths greater than 300 mμ, samples containing a variety of *p*-phenylenediamines swollen in from solutions containing 0.7×10^{-3} moles additive/mole rubber all showed a slight increase in degradation rate to begin with, but subsequently degradation was inhibited (Figure 3).

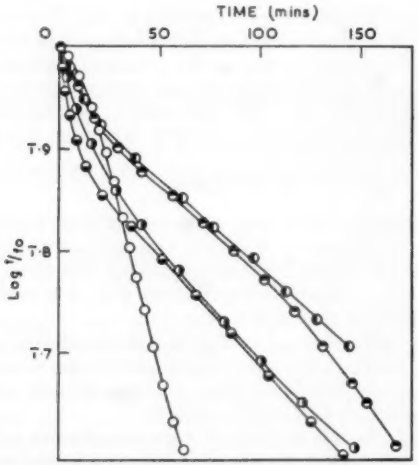

FIG. 1.—Comparison of the effect of various naphthylamines at a concentration of 0.7×10^{-3} moles/base mole rubber on the photolytic stress relaxation of a peroxide vulcanizate: (◓) phenyl-α-naphthylamine; (◒) phenyl-2-naphthylamine; (◐) α,β-dinaphthylamine; (◑) β,β-dinaphthylamine; (○) no additive.

The *p*-phenylenediamines employed were N,N′-diphenyl-*p*-phenylenediamine (D.P.P.D., Monosanto Ltd.), N,N′-di-*sec*-butyl-*p*-phenylenediamine (Topanol M, I.C.I. Ltd.), N,N′-dicyclohexyl-*p*-phenylenediamine (A.B. 129, I.C.I. Ltd.), N-cyclohexyl-N′-phenyl-*p*-phenylenediamine (Antioxidant 4010, J. M. Steel & Co.), N-phenyl-N′-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine (Universal Oil Products Ltd.), N,N′-di-3-(5-methylheptyl)-*p*-phenylenediamine

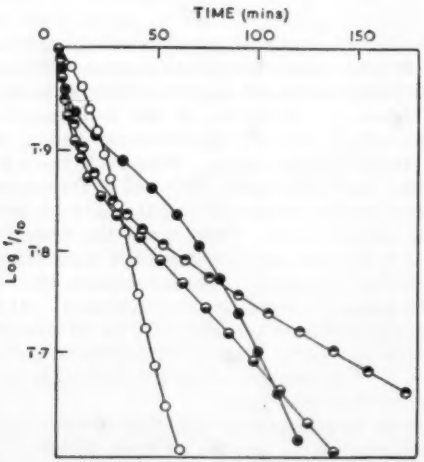

FIG. 2.—The effect of varying the concentration of phenyl-β-naphthylamine on the photolytic stress relaxation of a peroxide vulcanizate: (○) no additive; (●) 0.35×10^{-3} moles; (◓) 0.7×10^{-3} moles; (◒) 1.4×10^{-3} moles amine/base mole rubber.

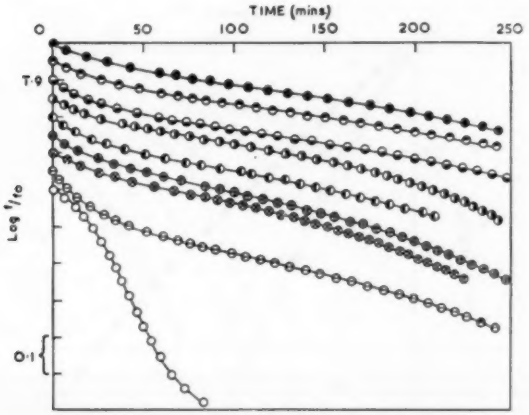

FIG. 3.—The influence on the photolytic stress relaxation of a peroxide vulcanizate of various *p*-phenylenediamines introduced by swelling in ethyl acetate solutions (0.7×10^{-3} moles amine/base mole rubber): (●) (N,N′-diphenyl-*p*-phenylenediamine; (◓) N,N′-dicyclohexyl-*p*-phenylenediamine; (◒) N,N′-di-3-(5-methylheptyl)-*p*-phenylenediamine; (◑) N,N′-di-*sec*-butyl-*p*-phenylenediamine; (◐) N-cyclohexyl-N′-phenyl-*p*-phenylenediamine; (⊕) N-phenyl-N′-(1-ethyl-3-methylpentyl)-*p*-phenylenediamine; (⊗) N,N′-di-2-octyl-*p*-phenylenediamine; (⊖) N,N′-dimethyl-N,N′-di-(1-methylpropyl)-*p*-phenylenediamine; (○) no additive. (Successive curves have been displaced vertically 0.5 unit.)

(Tenamene 31, Eastman Kodak Ltd.), N,N′-di-2-octyl-*p*-phenylenediamine (Tenamene 30, Eastman Kodak Ltd.), and N,N,′-di-methyl-N,N′-di-(1-methylpropyl)-*p*-phenylenediamine (Eastozone 32, Eastman Kodak Ltd.). The inhibited rate was of the same order with all these additives, and at this stage the strips were highly colored; in all cases degradation speeded up once more after about 200 minutes, and the color had by then been discharged. The initial acceleration of degradation was serious only in the case of N,N′-dimethyl-N,N′-di-(1-methylpropyl)-*p*-phenylenediamine, in which all the amine hydrogens were substituted.

In contrast with the *p*-phenylenediamines, diphenylethylenediamine has no initial deleterious effect on aging under 313 mμ irradiation, nor does it give rise subsequently to any inhibition period (Figure 4). Its effect is merely to reduce degradation rate about twofold throughout.

PHENOLS

In presence of phenolic antioxidants introduced by swelling from 0.2% solutions the relaxation data vary according to the additive employed (Figure 5). β-Naphthol and 4,4′-butylidenebis(6-*tert*-butyl-3-methylphenol) (Santowhite powder, Monsanto Ltd.) acted only as weak retarders of degradation, and there was only a short inhibition period in presence of α-naphthol and 4,4′-thiobis(6-*tert*-butyl-3-methylphenol) (Santowhite crystals, Monsanto Ltd.). 2,5-Di-*tert*-amylhydroquinone (Santovar A, Monsanto Ltd.), reduced degradation to a very low rate for 150 minutes, but after that time relaxation speeded up, while protection continued for more than 250 minutes in presence of 2,6-di-*tert*-butyl-4-methylphenol (Topanol O, I.C.I. Ltd.) and 2,4-dimethyl-6-*tert*-butylphenol (Topanol A, I.C.I. Ltd.), 2,2′-methylenebis-(4-methyl-6-*tert*-butylphenol) (Antioxidant 425, Cyanamid Corp.), 2,2′-methylenebis(4-ethyl-6-*tert*-butylphenol) (Antioxidant 2246, Cyanamid Corp.), and 2,2′-thiobis(6-methyl-

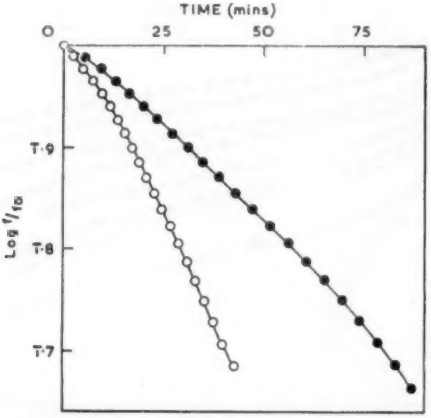

FIG. 4.—The effect of diphenylethylenediamine on the photolytic stress relaxation of a peroxide vulcanizate: (●) diphenylethylenediamine (0.7×10^{-3} moles/base mole rubber); (○) no additive.

phenol) (Santowhite C.M., Monsanto Ltd.); approximately the same steady relaxation rate was attained in presence of all these materials. In presence of Antioxidant 425, Antioxidant 2246, Santowhite C.M., and Topanol O, all relatively colorless and nonstaining antioxidants, the initial rate of degradation was greater than the steady rate subsequently attained.

DITHIOCARBAMATES, DITHIOPHOSPHATES, AND XANTHATES

A number of dibutyldithiocarbamates were tested as antioxidants in light of wavelength exceeding 300 mμ by introduction into peroxide vulcanizates by

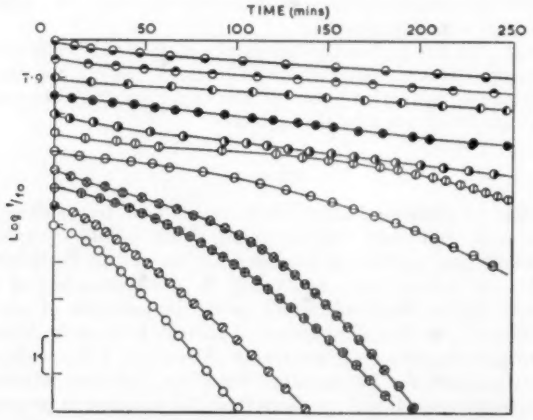

FIG. 5.—Comparison of the effect of various phenolic antioxidants introduced by swelling from 0.2% ethyl acetate solution on the photolytic stress relaxation of a peroxide vulcanizate: (◒) 2,2′-methylenebis-(4-methyl-6-*tert*-butylphenol); (◓) 2,2′-methylenebis(4-ethyl-6-*tert*-butylphenol); (◐) 2,4-dimethyl-6-*tert*-butylphenol; (●) 2,2′-thiobis(6-methylphenol); (◑) 2,6-di-*tert*(butyl-4-methylphenol; (◫) 2,5-di-*tert*-amyl hydroquinone, (⊖) 4,4′-thiobis(6-*tert*-butyl-3-methylphenol); (⊗) α-naphthol; (⊕) 4,4′-butylidene-bis-(6-*tert*-butyl-3-methylphenol); (⊘) β-naphthol; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

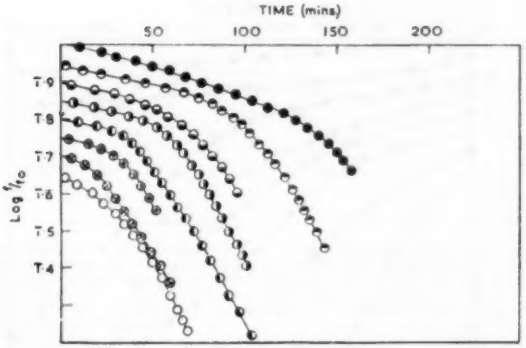

FIG. 6.—Comparison of the effect of various dibutyldithiocarbamates introduced by swelling from 0.2% ethyl acetate solution on the photochemical stress relaxation of a peroxide vulcanizate: (●) Ni; (◓) Pb; (◒) Zn; (◑) Cd; (◐) dibutylammonium; (⊕) Ba; (⊗) dimethylcyclohexylammonium; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

swelling from 0.2% solutions of the metal salts or 0.3% solutions of the alkylammonium salts. Many of them reduced the rate of relaxation to a low steady value, independent of the nature of the cation, from the commencement of irradiation (Figure 6). In no case was the protection very long-lived; the nickel salt, which was the most stable, protected for only 150 minutes. The lifetimes decreased in the following order: Ni > Pb > Zn > Cd > dibutylammonium > Ba > dimethylcyclohexylammonium. Copper and cobalt dibutyldithiocarbamates reduced the initial relaxation rate, but to a lesser extent than the foregoing, while the iron salt had a somewhat deleterious effect.

Nickel, zinc, and lead diisopropyldithiophosphates also afforded a marked initial protection against light aging but it was short-lived (Figure 7).

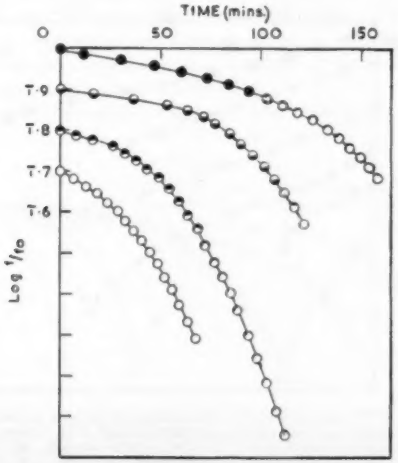

FIG. 7.—Comparison of the effect of various diisopropyldithiophosphates introduced by swelling from 0.2% ethyl acetate solutions on the photochemical stress relaxation of a peroxide vulcanizate: (●) Ni; (◒) Zn; (◓) Pb; (○) no additive.

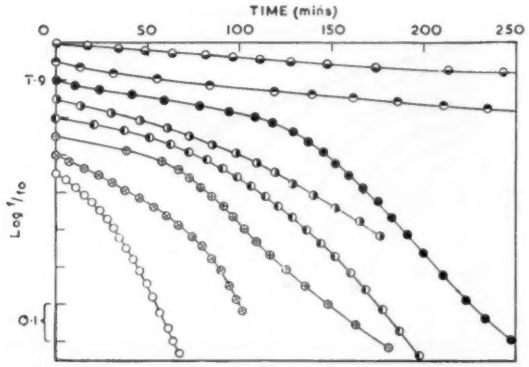

FIG. 8.—Comparison of the effect of various isopropylxanthates introduced by swelling from 0.2% ethyl acetate solution on the photochemical stress relaxation of a peroxide vulcanizate: (◒) Ni; (◓) Cr; (●) Sb; (◑) Mn; (◐) Co; (⊕) Zn; (⊗) Pb (○); no additive. (Successive curves have been displaced vertically by 0.1 unit.)

The effect of metal isopropylxanthates swollen in from 0.2% solution in ethyl acetate varied considerably according to the nature of the cation (Figure 8). The zinc, antimony, chromium, and nickel salts initially had a powerful inhibiting effect, but the induction periods for the Zn and Sb salts were only 50 and 100 minutes, respectively. The Ni and Cr salts remained active for at least 300 minutes, and data obtained on another sample of rubber (Figure 11) showed the induction period in presence of nickel isopropylxanthate to be 700 minutes. The relaxation rate was not so markedly reduced by the palladium and bismuth isopropylxanthates, although the effect of the former was long-lived, and the lead salt merely gave rise to a slight retardation in relaxation rate.

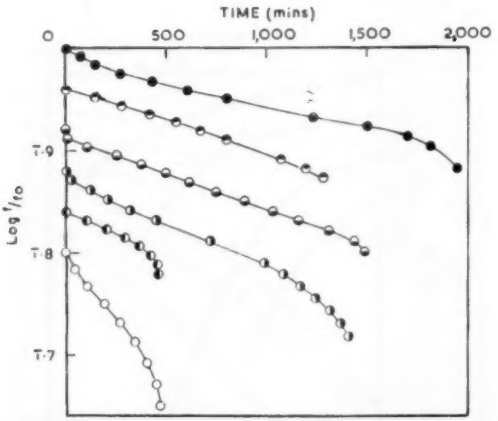

FIG. 9.—Comparison of the improvement in photochemical aging of a peroxide vulcanizate brought about by combining 2,2′-methylenebis(4-ethyl-6-*tert*-butylphenol) with various ultraviolet absorbers, all additives being introduced by swelling from a 0.2% ethyl acetate solution: (●) Tinuvin P; (◓) 2-hydroxy-4-methoxybenzophenone; (◒) 2,2′-dihydroxy-4-*n*-octoxybenzophenone; (◑) 2,2′-dihydroxy-4-methoxybenzophenone; (◐) M.D. 738; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

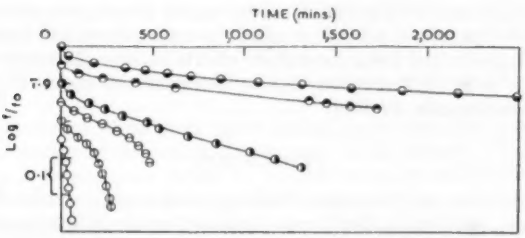

FIG. 10.—Comparison of the effect of Tinuvin P on the photochemical aging of a peroxide vulcanizate in presence of phenolic antioxidants, additives having been introduced by swelling from 0.2% ethyl acetate solutions: (◒) 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) +Tinuvin P; (◓) 2,2-methylenebis(4-ethyl-6-*tert*-butylphenol) +Tinuvin P; (◑) 2,5-di-*tert*-amyl hydroquinone +Tinuvin P; (⊖) 2,2′-methylenebis(4-ethyl-6-*tert*-butylphenol); (◫) 2,5-di-*tert*-amyl hydroquinone; (○) no additive. (Successive curves have been displaced vertically by 0.05 unit.)

ULTRAVIOLET ABSORBERS

The commercial absorbers of ultraviolet light Tinuvin P, a benzotriazole derivative of undisclosed composition (Geigy Ltd.), U.V. 9 (2-hydroxy-4-methoxybenzophenone), U.V. 24 (2,2′-dihydroxy-4-methoxybenzophenone), and U.V. 314 (2,2′-dihydroxy-4-*n*-octoxybenzophenone) (Cyanamid Corp.) all reduced the rate of photolytic degradation of peroxide vulcanizates slightly in the absence of added antioxidant. In combination with 0.2% antioxidant 2246, 0.2% of any of these ultraviolet absorbers dramatically reduced the rate of photochemical degradation and improved the lifetime of the antioxidant (Figure 9), Tinuvin P being the most effective. M.D. 738, whose formula is unknown, also reduced the rate of aging but did not improve the lifetime of the antioxidant. The protective effect of phenolic antioxidants 2246 or 425 in combination with Tinuvin P was far greater than that of the antioxidants alone (Figure 10). In presence of Antioxidant 425 and Tinuvin P the initial rate of degradation was faster than in presence of Antioxidant 2246 and Tinuvin P, but the steady rate of relaxation subsequently attained was somewhat slower. This effect could also be seen when these antioxidants were compared in absence of Tinuvin P (Figure 5), but it was not then so striking. In presence of Santovar A, which by itself was not very stable, the lifetime of the antioxidant was much prolonged by addition of ultraviolet absorber.

Tinuvin P did not appreciably improve the protection afforded by nickel

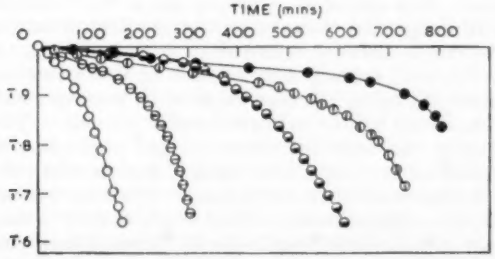

FIG. 11.—The effect of Tinuvin P on the photochemical aging of a peroxide vulcanizate containing zinc and nickel dibutyldithiocarbamates; additives having been introduced by swelling in 0.2% ethyl acetate solutions: (●) nickel dibutyldithiocarbamate +Tinuvin P; (◫) nickel dibutyldithiocarbamate; (◒) zinc dibutyldithiocarbamate +Tinuvin P; (⊖) zinc dibutyldithiocarbamate; (○) no additives.

dibutyldithiocarbamate (Figure 11) or by nickel isopropylxanthate, although it did improve the rate of relaxation after the antioxidant had been exhausted. Nor did it improve the weak inhibitory effects of zinc diisopropyldithiophosphate or zinc isopropylxanthate, but it increased the useful lifetime of zinc dibutyldithiocarbamate fivefold.

DISCUSSION

Naphthylamines photosensitize the degradation of peroxide vulcanizates in light of wavelength 300 mμ and greater just as they do in 365 mμ light[1], but the relative increase in degradation rate is smaller because the vulcanizate itself absorbs strongly at 300 mμ and relaxes rapidly in the absence of additive. The existence of an optimum concentration (0.7×10^{-3} moles/base mole rubber) of PBN, which causes the most serious degradation, is evident once again. The amount of photosensitization does not, as might be expected, increase continuously with increasing PBN concentration, because a protective effect becomes obvious as relaxation proceeds, and this is more pronounced at higher concentrations. This effect was originally considered to be due to absorption of all radiation by PBN near to the surface of the vulcanizate, so that the rubber in this region was completely degraded while the underlying material remained undegraded and continued to support stress. In such an event, relaxation should cease once the outer layers have completely degraded, but in fact it slowed down to a steady rate and eventually accelerated again (Figure 2). During the slow stage the samples were highly colored, and this color disappeared as the rate speeded up, indicating that the eventual slowing down of relaxation must be due to a colored oxidation product of the naphthylamines, which subsequently is itself destroyed. PAN and α,β-dinaphthylamine, which are very susceptible to oxidation on storage, are less damaging in ultraviolet light than PBN and β,β-dinaphthylamine, and the latter, which does not readily discolor, gives the least efficient protection against light. The colored product might act either as a true antioxidant or as an ultraviolet absorber, the former being likely, since the ability of the oxidation products of PBN to act as antioxidants has previously been shown[6].

As had been predicted from an examination of their spectra[1], the *p*-phenylenediamines also initially accelerated stress relaxation but highly colored reaction products were rapidly produced, and the relaxation was inhibited until the color was discharged. All *p*-phenylenediamines had much the same effect upon light aging, but since they all gave rise to severe staining during their inhibitory period, they are of no practical use in light-colored vulcanizates. Le Bras[7] recently suggested that the protective effect of amines against light aging might be due to network reformation by crosslinking. The protective effect noted in this work and also that to which Le Bras refers[1] cannot be due to crosslinking, since the aging has been followed by measurement of continuous stress relaxation which follows network breakdown only. The possibility of crosslinking cannot be overlooked, however, and would be manifested in increased permanent set in samples after aging. A comparison of the permanent set of a control without additive and a sample which had contained N-phenyl-N′-cyclohexyl-*p*-phenylenediamine, both of which were 60% degraded, showed that the increase in unstretched length was 40% in each case; with other amines also, the amount of permanent set was found to depend only on the extent of degradation. Crosslinking cannot, therefore, be considered as an important factor in the protective effect of amines against light.

It has been suggested that diphenylethylenediamine might be a useful antioxidant at 313 mμ since it absorbs only slightly at this and at higher wavelengths[1]. However, although this additive does not accelerate degradation at 313 mμ it is of no value since it affords only slight protection throughout degradation.

The behavior of phenols as light antioxidants depends markedly on the position and nature of the substituent groups on the phenol. It appears essential that the *ortho* positions should be blocked so as to reduce the possibility of reactions at the hydroxyl group which would destroy the phenol uselessly. β-Naphthol with all *ortho* positions free is ineffective, while α-naphthol and Santowhite powder, both of which have one free *ortho* position, are only weak antioxidants in this system. Santovar A, which also has one free *ortho* position at each hydroxyl group, protects well against light aging, but its action is short-lived; in this case the substituent is bulky *tert*-amyl. In the remaining phenols, all the *ortho* positions were blocked, and all protected very well. Furthermore, none of them seriously discolored the rubber, although in no case did the rubber remain completely colorless; it appeared essential that some of the colored product should have appeared for the rate of aging to reach its minimum, since the rate of relaxation initially decreased and attained a low steady value.

The addition of ultraviolet absorber Tinuvin P still further reduced the rate of relaxation in presence of a hindered phenol (Figure 10), and the results obtained by combining Tinuvin P and Santovar A show that the presence of ultraviolet absorber also prolongs the life of the antioxidant. It is much more obvious from the results obtained in presence of Tinuvin P that the maximum inhibition is not exhibited until some stain has appeared in the rubber. The technological importance of the combination of ultraviolet absorbers with hindered phenolic antioxidants has already been discussed[8], and it is now clear that those absorbers which are derived from benzophenone compare fairly well with Tinuvin P (Figure 9).

It has already been pointed out that a variety of dialkyldithiocarbamates act as antioxidants in rubber irradiated with 365 mμ light[2], although some of them are short-lived. This was also true in light of shorter wavelengths (Figure 6), but the lifetime of dithiocarbamate introduced from 0.2% solution was only about 50 minutes. The inhibited rate was independent of the cation, but the lifetime varied, the nickel dibutyldithiocarbamate being the longest lived. Metal diisopropyldithiophosphates also protected against 313 mμ light for a short while, but none of these materials were sufficiently long-lived to be useful in practice.

Nickel isopropylxanthate, which has been advocated as a very efficient protective agent in light[9], does indeed compare very favorably with hindered phenols without added ultraviolet absorber (Figure 8); it is not, however, improved by the addition of Tinuvin P. This protective action is not specific to the nickel salt, as has previously been implied, for equally good results were obtained with chromium isopropylxanthate, while the antimony, manganese, cobalt, and zinc salts reduced relaxation to the same inhibited rate, although they were somewhat short-lived. Palladium and bismuth salts retarded relaxation as if they were acting as ultraviolet absorbers. It was conceived that the stability of the nickel and chromium salts might be due to the formation of complexes, but this seems unlikely in view of the fact that neither cobalt nor manganese isopropylxanthates have long-lived protective action. Karmitz[9] suggested that the protective role of nickel isopropylxanthate is partially that

of an ultraviolet absorber, and, while this cannot be its only mode of protection, since it is known that many dithiocarbamates including that of nickel protect against thermal as well as photolytic aging, the fact that the nickel salt is particularly long-lived may be due to its absorbing harmlessly radiation which would otherwise cause the rubber to oxidize and necessitate the intervention of the nickel salt as a true antioxidant. Some evidence that the nickel salts do, in fact, act as ultraviolet absorbers has been obtained by comparing the effect of Tinuvin P on samples containing zinc and nickel dibutyldithiocarbamates (Figure 11). Addition of Tinuvin P to a sample containing the zinc salt markedly reduced the inhibited rate and extended the period of inhibition, whereas in presence of the nickel salt addition of Tinuvin P effected no substantial improvement in relaxation rate or inhibition period. As stated above, Tinuvin P is also without effect in the presence of nickel isopropylxanthate, which suggests that these nickel salts are already acting as ultraviolet absorbers, as well as antioxidants.

SYNOPSIS

The oxidative degradation of peroxide vulcanized natural rubber at wavelengths of 300 mμ and above has been studied by the technique of stress relaxation. Substituted naphthylamines and *p*-phenylenediamines, particularly the former, initially photosensitize the degradation of the vulcanizate but subsequently give rise to colored products which act as antioxidants. The protective action of these amines is not due to network formation. Completely hindered phenols have been shown to be powerful antioxidants of long life, but nonhindered phenols are not good antioxidants against light. The combination of an ultraviolet absorber with a hindered phenol gives excellent protection which is only fully developed when a little of the phenol has been oxidized to a colored compound. Many dithiocarbamates, dithiophosphates, and xanthates protect against light, but their effect is short-lived except in the case of nickel and chromium isopropylxanthates. The peculiar stability of these materials is attributed to their acting as both ultraviolet absorbers and antioxidants. Since the addition of ultraviolet absorber to the nickel and chromium xanthates does not further increase their effectiveness, the combination of a hindered phenol and an ultraviolet absorber is the most potent protective agent against light for incorporation into translucent rubber vulcanizates.

ACKNOWLEDGMENTS

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MODERN ROLE OF THE ELECTRON MICROSCOPE IN RUBBER RESEARCH *

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Until recently, the main role of the electron microscope in rubber research was the determination of particle size and shape of reinforcing pigments and fillers. The electron microscope proved its value in its first industrial problem in 1940[1] when it showed the particle size of Micronex to be 28 mμ. In 1942[2,3] it established the correlation between particle size of carbon and rubber properties. The next contribution was the establishment of reticulate chain structure, in 1945[4], using stereo-photomicrography. The electron microscope led the way to the carbon gel concept when carbons producing different road wear results were shown to have equal particle size and structure. Micrographs of carbon gel were published in 1951[5]. Studies of rubber latexes, various pigments and fillers were also applications of the electron microscope in which the determination of particle size and shape was involved.

Today, improvements in resolution, development of new techniques and accessory equipment have greatly expanded the application of the electron microscope. This paper is concerned mainly with describing these new developments; first, as a help to electron microscopists in the rubber field; second, to illustrate what can be done with the electron microscope, so that research and production men can recognize possible applications of this discerning tool to the solution of their problems.

Electron microscopes have come a long way in the short 20-year period. Figure 1 shows the microscope used in our laboratories. This instrument is currently resolving detail as fine as 10 A or 1 mμ in routine daily operation. Its design makes possible the development of special holders and thereby increases its value as a research tool.

Another piece of equipment that is as important in microscope research as the electron microscope itself is the evaporating unit shown in Figure 2. This is used for shadowing and forming replication films under vacuum, thus making possible studies of rubber surfaces and surfaces of pigments and other rubber ingredients. In shadowing, detail is made visible by coating the specimen with metal evaporated at an angle from the tungsten basket at A. Carbon can be evaporated by the arc at B, forming a replicating film or mold of the specimen. This will be discussed under "preparation".

Today, the proper *preparation of specimens* is the most important step in successful microscopy. The various preparations used are as follows.

Pigments and latexes.—A glass microscope slide is dipped in a solution of formvar in ethylene dichloride and allowed to dry. The pigment, e.g., carbon black, is dusted or rolled on the film using a Q-tip. The film is then floated on a water surface, a screen previously dipped in a film adhesive is placed on the film, and the screen and film removed from the water surface to dry. After dry-

* Presented before the Division of Rubber Chemistry, ACS, New York, September 1960.

FIG. 1.—Modern electron microscope.

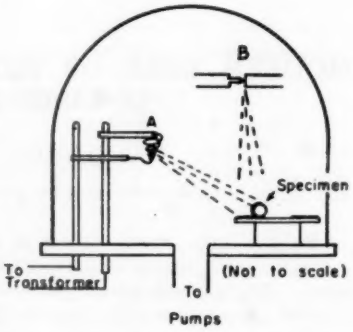

FIG. 2.—Evaporator.

ing, the specimen is given a coating of carbon, and evaporated under vacuum. This conducting film stabilizes the specimen under the electron beam by cutting down heat buildup and electrostatic charges, thus eliminating specimen drift.

Although many microscopists use carbon films or substrates instead of formvar, it has been our experience that thinner, stronger films for high resolution work can be obtained by the use of extremely thin formvar films, carbon coated. The formvar film should be so thin that it can hardly be seen when floated on a water surface; the carbon coating should be just enough to prevent drift. The dusted pigment makes the thin formvar film visible or, if only the substrate is required at this time, the screens can be placed on the formvar-coated slide before floating on a water surface. Also, if particle structure is to be studied, the sample should not be "sparked" or Tesla coil dispersed as we suggested in earlier publications. Present day resolution will show surface

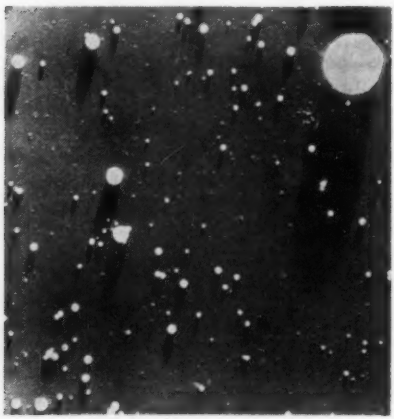

FIG. 3.—Hevea latex (×10,000).

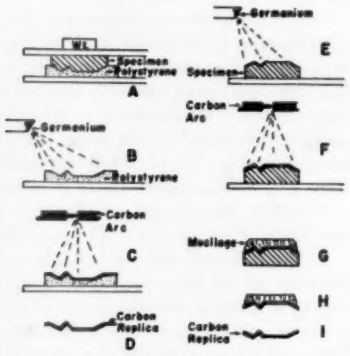

FIG. 4.—Replication.

structure changes produced by sparking. The use of the Q-tip eliminates this effect.

Rubber latexes have to be hardened while in suspension. The addition of a few drops of Clorox to the diluted latex will harden the particles uniformly. Figure 3 shows the large particles of hevea latex hardened to the same extent as the very small.

Replication.—Whereas previously, little replication was done in rubber research, today this is a vital technique. Usually the rubber specimen is frozen in liquid nitrogen and fractured. The fractured surface is replicated by either of the two techniques shown in Figure 4.

The rubber sample is first placed in contact with a polystyrene disc, as in A, and a 2–3 oz weight placed on top. The assembly is placed in an oven at 165° C for 5–10 minutes and then allowed to cool in the oven. The rubber is mechanically stripped from the polystyrene. The discs are placed in the evaporator. Detail is revealed by shadowing with germanium as in B, after which carbon is evaporated from the arc forming a replicating film over the

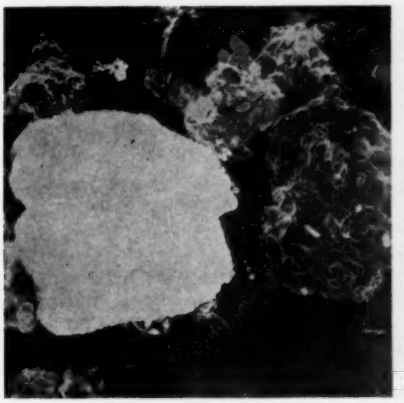

FIG. 5.—Clay (×7,500).

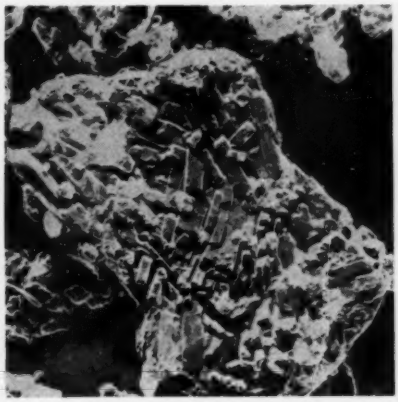

FIG. 6.—Mercaptobenzothiazole.

polystyrene surface as in C. The polystyrene disc is dissolved in ethylene dichloride, leaving the carbon replica as in D. For very rough surfaces in which large shadows may occlude much detail, the sample can be rotated under vacuum while being shadowed.

A higher resolution method of replication is also shown in Figure 4. The rubber specimen is placed under vacuum and shadowed as in E. The sample is carbon replicated as in F. The problem is to remove the fragile carbon replica from the rubber surface. This can be done by applying mucilage to the carbon replica, building it up as in G and then mechanically stripping the supported replica (H). The mucilage is dissolved away in water, leaving the shadowed carbon replica (I). If the mucilage swells unduly during dissolving, thus breaking the replica, a supporting film of wax can be applied to the replica, giving protection during removal of the mucilage. The wax is finally removed with xylene.

Replication of powders, etc.—Instead of a rubber surface, a powder may be substituted as in E, Figure 4. Following shadowing and replication, the

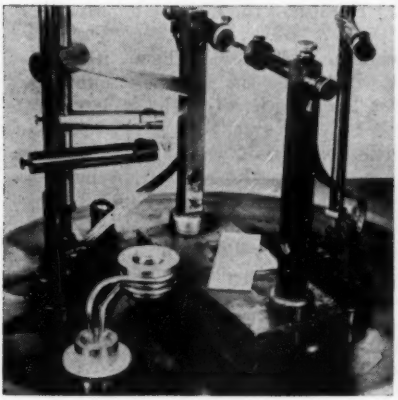

FIG. 7.—Freezing coil.

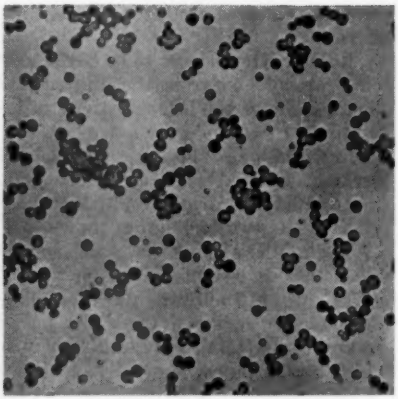

FIG. 8.—Low MP latex (×15,000).

powder is removed by a suitable solvent. If this solvent is an acid, then platinum has to be used in place of germanium for shadowing. Figure 5 shows the advantage of replication. The large white mass represents a clay aggregate that has not been dissolved. To the right, a replica from which all clay has been dissolved is seen, thus revealing the many fine crystal platelets comprising the sample.

In all replica work it is recommended that stereo-micrography be used. This technique is vital for successful interpretation.

Study of low melting point materials.—The heating effect of the electron beam, which averages from 125° C–300° C, depending on intensity and sample preparation, makes the examination of low melting point materials difficult. The heating effect of the arc in the evaporator, although less than that encountered in the microscope, likewise limits the replication of some materials. Many low melting point materials can be replicated by first evaporating a coat-

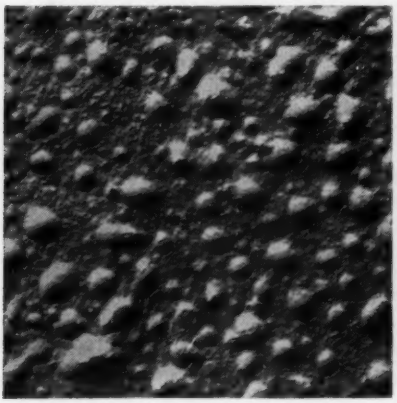

FIG. 9.—Dipped latex goods (×7,500).

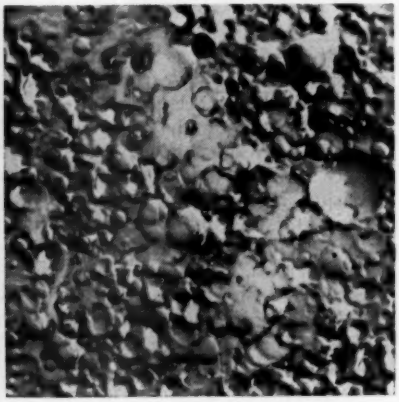

FIG. 10.—FT in hevea (×7,500).

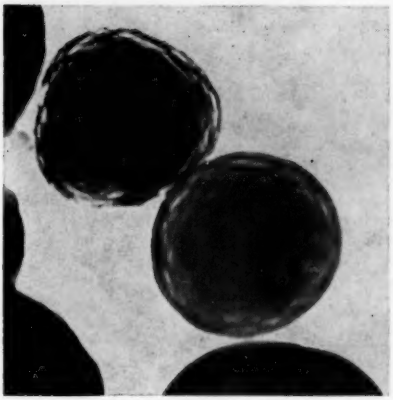

FIG. 11.—Layered structure in MT (×100,000).

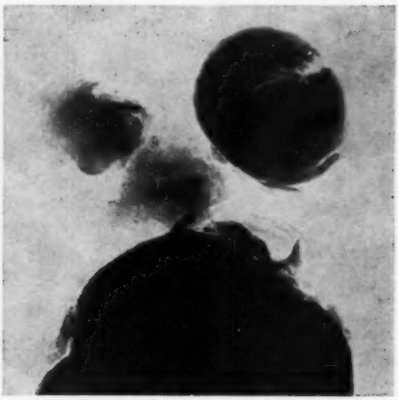

FIG. 12.—Broken MT particle (×100,000).

ing of aluminum on the specimen which then protects the sample from the heat of the carbon arc. Figure 6 shows an accelerator, mercaptobenzothiazole, prepared by this method.

Materials with a melting point as low as 50° C can be replicated by first freezing, then shadowing and replicating while still frozen. Figure 7 shows a freezing coil built for the evaporator. The unit is cooled by circulating liquid nitrogen through the coil. Figure 8 shows a polymer latex with melting point below 50° C prepard by this technique.

Additional examples of *applications* of the electron microscope to rubber research follow.

Figure 9 shows the surface of dipped mechanical goods. This, as well as micrographs of torn interior surfaces, have proven that latex particle size persists in the cured product. Actually, the size of the original latex used could be determined from such prints.

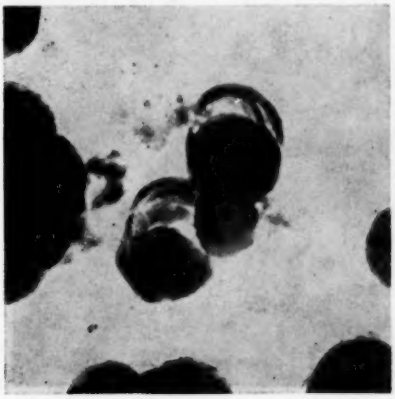

FIG. 13.—Separated layers—MT (×100,000).

FIG. 14.—Cross-section of MT particle (×200,000).

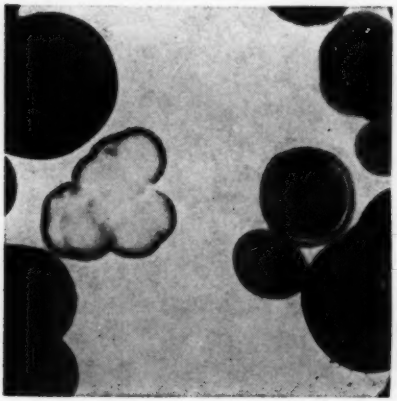

FIG. 15.—Acid oxidation—MT (×100,000).

FIG. 16.—Porosity in MT (×200,000).

Figure 10 shows the dispersion of FT carbon in hevea. The rubber was frozen in liquid nitrogen, fractured, shadowed and replicated with evaporated carbon. The carbon replica was stripped with mucilage as described above. The clean break between carbon and rubber is shown.

Carbon blacks.—The thermal blacks provide an interesting study especially if micrographs are taken at 100 KV. Figure 11 shows a layered formation in the MT particles. In Figure 12, a particle fractured by ball milling shows layering in the break. The "onion skin" peeling is quite evident in Figure 13. In Figure 14 a fragment of MT shows a cross-sectional view of the particle. The angularity in the particle contour and the layers should be noted. Ball milling of other blacks should provide valuable information on the actual formation of the carbon black particles under various furnace conditions.

Oxidation by acid is shown in Figure 15. Once entry to the particle is

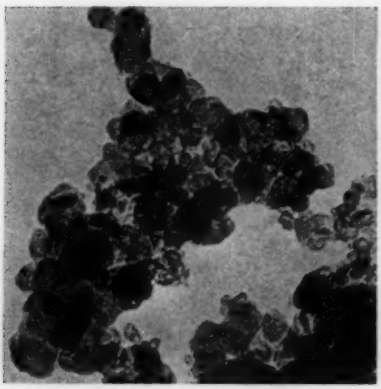

FIG. 17.—Surface oxidation—HAF (×200,000)

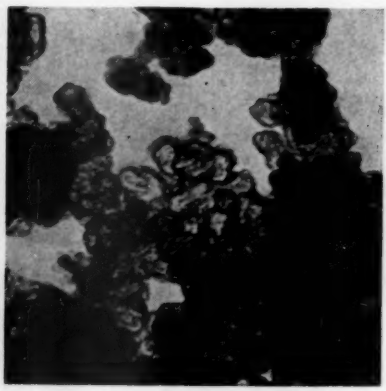

FIG. 18.—Oxidation-Commercial ISAF (×200,000).

FIG. 19.—Contamination (×100,000).

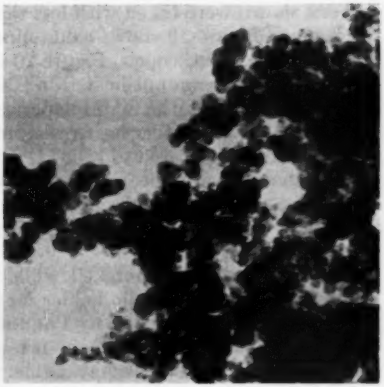

FIG. 20.—Elimination of contamination by high temperature (×100,000).

made, the center is completely removed. The particle at the right shows the beginning of this process.

Porosity in carbon is shown in Figure 16; the pores measure 10 A in size. Surface crystallinity is also indicated.

Figure 17 shows the effect of surface oxidation on an HAF black. This same effect has been observed in color blacks with average particle sizes below 10 mμ. A high degree of oxidation in a commercial ISAF black is shown in Figure 18.

Special holders.—We have developed special holders for the electron microscope. One of these permits heating the sample while being observed on the screen of the microscope. A major difficulty, particularly with carbon blacks is contamination buildup in the microscope. Most of the micrographs of

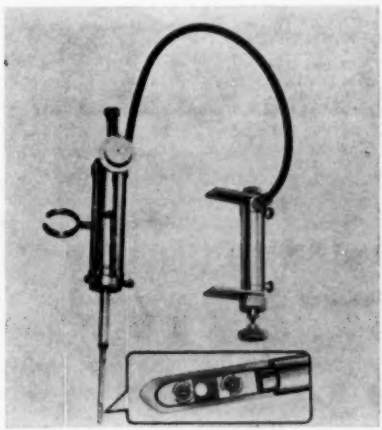

FIG. 21.—Tensile holder.

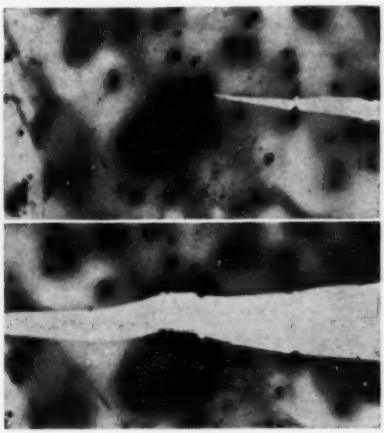

FIG. 22.—Crack growth in rubber on stretching (×8,500).

carbons shown were taken with less than 15 seconds exposure of the sample to the beam. Figure 19 shows contamination buildup on an ISAF black in one minute in the microscope. Figure 20 shows the same carbon after 30 minutes exposure to the beam but heated to 600° C during exposure. This elimination of contamination by the high temperature holder is a major advance in studies of carbon black and other heat resistant materials. Our present high temperature holder can be heated to 1500° C with the prospects of even higher temperatures. In addition to heating the specimen, air or other gases can be admitted during observation. Low temperature holders cooled with liquid nitrogen are also under development and will permit examination of low melting point materials directly.

Specimens can be stretched while under observation in the microscope.[6] Figure 21 shows the tensile holder for this operation. The sample is held by the fixed jaw and stretched by the movable jaw shown at the right. An hydraulic system allowing constant rate deformation studies and extremely fine control of the sample is also available. Rubber samples for such studies must be kept thin and given a carbon film coating to prevent heat embrittlement under the beam. New pointed filaments[7] and cooling while stretching will permit the study of thicker films. The growth of a crack in a thin rubber film is shown in Figure 22 and indicates a clean break between carbon and rubber.

In summary, the electron microscope is no longer only a tool to measure particle size and shape. High resolution, new techniques and accessories have changed this. Microscope studies today are concerned with the carbon particle itself, the detection of oxidation effects, heat treatment effects, etc. New holders permit such studies right in the microscope: tensile holders permit dynamic studies in the microscope. Replication techniques make possible studies on rubber dispersions, low melting point materials, aggregates etc. All these advances have opened a new promising field for electron microscope research. Careful preparation and controlled studies will aid and advance the knowledge of reinforcement to a degree never before anticipated.

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THERMAL EXPANSION MEASUREMENTS AND TRANSITION TEMPERATURES. II. AN AUTOMATIC RECORDING SYSTEM

MARK L. DANNIS

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A differential expansion apparatus useful for studying first- and second-order transitions in polymeric materials was described[1] in paper I. This apparatus utilizes a tipping mirror arrangement as part of an optical lever to magnify the expansion of the polymer sample with a change in temperature. Readings of light spot position on a scale and of sample temperature had to be taken almost continuously to obtain useful curves. These readings were very tedious and time-consuming, limiting the usefulness of the technique. Hence, an automatic recording system was developed, greatly expanding the potentialities of this kind of analysis.

The apparatus currently in use is illustrated in Figure 1. An *X-Y* recorder (Electronic function plotter, Minneapolis Honeywell, Brown Instrument Division) replaces the galvanometer scale shown in Figure 4 of reference 1.

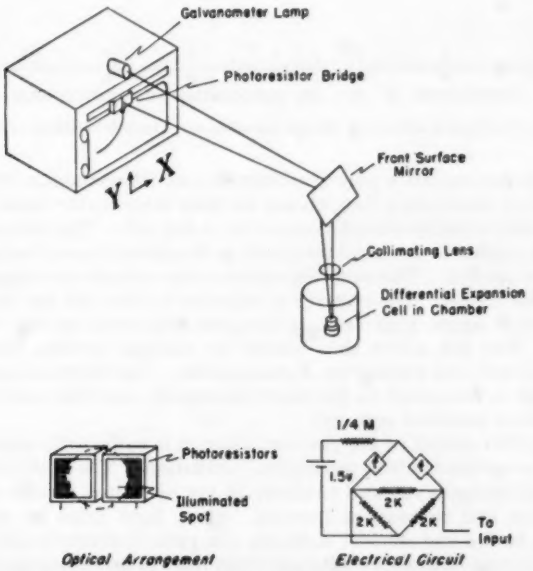

FIG. 1.—Schematic arrangement of expansion apparatus with details of photoresistor arrangement.

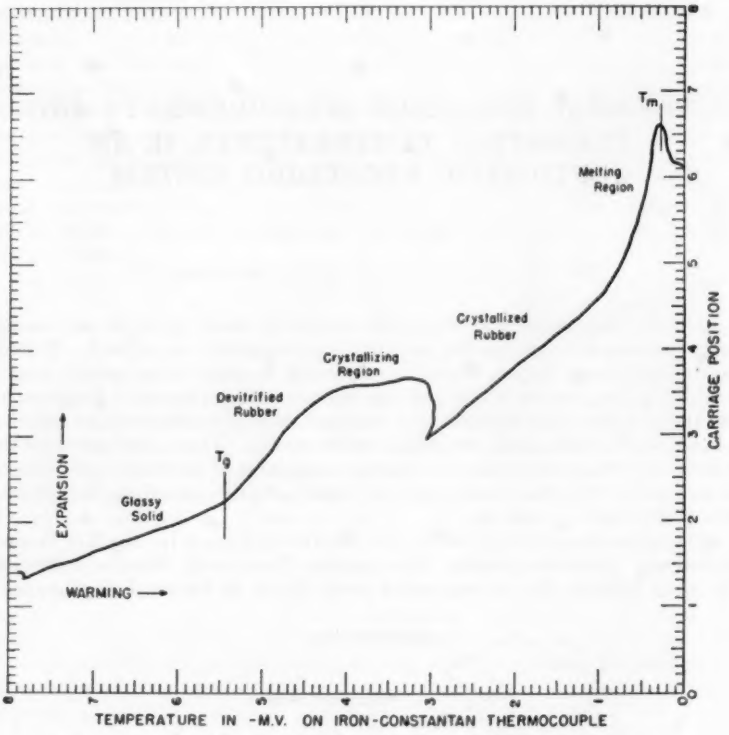

FIG. 2.—Typical differential thermal expansion curve for polybutadiene rubber.

The carriage pen carries a pair of photoresistors (Powermaster Photocell No. CDS-10, Hupp Electronics Co.), chosen for their large surface area. These are part of a resistive bridge circuit powered by a dry cell. The output voltage of the bridge is applied to the input terminals on the pen carriage after its potentiometer power is opened. This rewiring replaces the normal error signal with the output of the bridge. The polarity is adjusted so that the pen movement reduces the error signal, thus keeping the photocell bridge at the center of the light spot. The pen motor thus moves the carriage system, both centering the photocell unit and tracing the X component. The thermocouple imbedded in the sample is connected to the chart movement amplifier controlling the Y component in a standard manner.

The amplifier circuit in the pen servo circuit is sufficiently sensitive that it can easily be overloaded into mechanical oscillation. The potential applied to the photocell bridge is reduced to about 10 mv by a drop resistor to eliminate this overdrive and subsequent hunting. Stray light must be reduced with appropriate baffles and shields; however, complete darkness is not required.

A typical expansion curve obtained from this revised apparatus is shown in Figure 2. This curve is for a sample of uncured polybutadiene, about 98% in the *cis*-1,4 configuration. The sample in the expansion cell was precooled with

liquid air, beginning the run. Warmup from about −8 mv to −5.4 mv (−110° C) is linear and typical of a glassy organic solid. The change in slope defines T_g. Warmup to about −4.5 mv is characteristic of a devitrified rubber. At about −4 mv (−85° C) crystallization begins, with liberation of heat, which further accelerates the process to exhaustion. The warm sample cools slightly, then expands linearly to about −1 mv (−20° C), wherein melting begins. The melting point, T_m, is evident at −0.2 mv −(4° C), above which linear expansion again can be noted. Frozen stresses account for the apparent shrinkage just above the melting point.

While the work reported thus far in this note and in reference 1 has covered only the temperature range below room temperature, the range above room temperature can be studied easily by replacing the Dewar system with a small oven, heated at a controlled rate. Studies typical of this latter kind are illustrated by glassy changes in polyvinyl chloride at about +85° C and by crystalline melting points in polyethylenes about 130° C. Most polymers studied at higher temperatures are too low in molecular weight to show simple rubbery expansion above either T_g or T_m. Instead, at the higher temperatures, they generally creep or flow rapidly, apparently indicating contraction. Cooling curves from very high temperatures can be obtained if the mirror tripod is properly adjusted or compensated for the expected creep.

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DETERMINATION OF DEGREE OF CROSSLINKING IN NATURAL RUBBER VULCANIZATES. PART III

L. MULLINS

Attention is called to several errors in the paper by Dr. Mullins, pages 279–289 in the preceding issue of RUBBER CHEMISTRY AND TECHNOLOGY.

On page 286 in the sentence just below Figure 5 "follow" should read "follows" and Equation (7) should read

$$N_e = (N \text{ chemical} + N \text{ entanglements}) \times (1 - \beta M_e M^{-1}) \qquad (7)$$

Just below Equation (9) on page 287 "Figure 5" should read "Figure 6". In the first line below Figure 6 on page 287 "M^{-1*}" should read "M_e^{-1*}" and in the third line below Figure 6 "$C_1^{\infty *} = \frac{1}{2} \rho RTM_e^{*}$" should read "$C_1^{\infty *} = \frac{1}{2} \rho \mathrm{R}\mathrm{T}M_e^{-1*}$".

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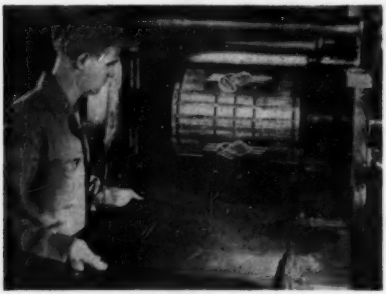

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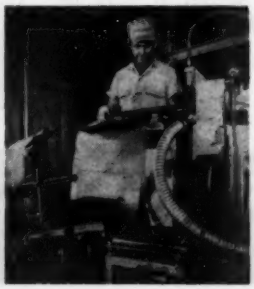

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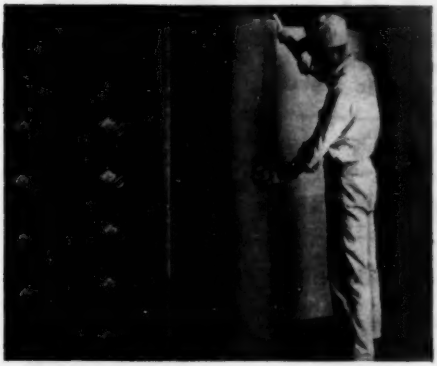

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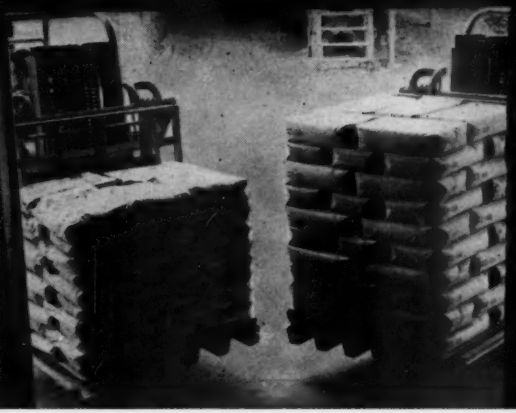

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